MINISTRY OF THE ENVIRONMENT

ISSN 0-825-4591

STANDARDS DEVELOPMENT BRANCH OMOE
3 6936 00000 2424

PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE

December 8 & 9, 1986

THE SHERATON CENTRE
TORONTO, ONTARIO,
CANADA

Part C
Liquid & Solid Waste Research

TD
172.5
.057
1986
part C
MOE

DATE DUE

TD
172.5
.O57
1986
part C

Proceedings : technology
transfer conference

76021

ISSN 0-825-4591

TD
172.5
O57
1986
v.4

PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE

December 8 & 9, 1986

The Sheraton Centre

External Research Projects

PART C
LIQUID & SOLID WASTE RESEARCH

Organized by
Research Advisory Committee

Sponsored by

Corporate Resources Division
Ministry of the Environment
Ontario
CANADA

Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact Service Ontario Publications at copyright@ontario.ca

Goal Statement

"To achieve and maintain a quality of the environment - including air, water and land - that will protect human health and the ecosystem and will contribute to the well-being of the people of Ontario."

ACKNOWLEDGEMENTS

The Conference Committee would like to thank the speakers and organizers for their valuable contributions.

DISCLAIMER

The views and ideas expressed in these papers are those of the authors and do not necessarily reflect the views and policies of the Ministry of the Environment, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

INTRODUCTION

The Ontario Ministry of the Environment holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario universities and by private research organizations.

The papers presented at the Technology Transfer Conference held in December 1986 are presented in Conference Proceedings. These Proceedings are divided into five parts corresponding to the conference sessions dealing with:
Part A: Air Quality Research ;
Part B: Water Quality Research;
Part C: Liquid & Solid Waste;
Part D: Analytical Methods; and
Part E: Environmental Economics.

This part is a collation of those papers presented at Session C of the Conference.

For further information on any of the projects, the reader is kindly referred to the Principal Investigators or to the Research Management Office at (416) 965-5788.

Paper No. **Page No.**

INTRODUCTION

PART A: AIR QUALITY RESEARCH:

FEATURE PAPERS

A AN OVERVIEW OF ALBERTA ENVIRONMENT'S DEPOSITION RESEARCH PROGRAM 1
H.P. Sims: Director, Alberta Environment's Research Management Division, Alberta, Canada.

B MULTIMEDIA ANALYSIS AND ASSESSMENT OF ENVIRONMENTAL TOXIC AND CARCINOGENIC SUBSTANCES ... 29
R. Harkov: Office of Science and Research, New Jersey Dept. of Environmental Protection, New Jersey, U.S.A.

SESSION PAPERS

1 THE RAPID SCREENING OF MUNICIPAL REFUSE INCINERATOR FLYASH AND STACK GAS FOR PCDD/PCDF USING A TRANSPORTABLE TANDEM MASS SPECTROMETER (GC/MS/MS) SYSTEM 45
B. Shushan[1], A. Ngo[1], V. Ozvacic[2], G. Wong[2], G. DeBrou[2], B. Bobbie[2], R. Clement[2], S. Thorndyke[3] and B. Chittum[4]. 1-SCIEX, 2-Environment Ontario, 3-ORF, 4-Willington Consultants.

2 RETROSPECTIVE CORRELATION SPECTROSCOPY AND ITS APPLICATION TO ATMOSPHERIC MONITORING 59
R.W. Nicholls, M. Amani, M. Mandelman and W. Morrow, York University, Toronto, Ontario.

3 MEASUREMENT OF ATMOSPHERIC CONSTITUENTS BY TUNABLE DIODE LASER ABSORPTION SPECTROMETRY 64
H.I. Schiff, York University, Toronto, Ontario.

4 UPTAKE, DISTRIBUTION AND CLEARANCE OF SOLUBLE AEROSOLS IN THE HUMAN RESPIRATORY SYSTEM 81
W.J. Megaw[1] and J.F. Hicks[2]. 1-York University, Toronto, and 2-Environment Ontario.

5 EXPERIMENTALLY DETERMINED MUTATION RATES IN LUNG AS AN AIR QUALITY STANDARD 92
J. Heddle, A. Bouch, C. Couch, H. Kaul, J. Gingerich and K. Jain, York University, Toronto, Ontario.

Paper No. **Page No.**

6 **THE HAMILTON STUDY: EFFECTS OF FINE PARTICLES ON THE RESPIRATORY HEALTH OF SCHOOL CHILDREN** 106
L.D. Pengelly, A. Kerigan, C. Goldsmith,
W. Furlong and S. Toplack, McMaster University,
Hamilton, Ontario.

7 **BIOLOGICAL MONITORING OF ENVIRONMENTAL GENOTOXICITY** 134
M. Petras, J. Norsworthy, M. Vrzoc, and K. Hill,
University of Windsor, Windsor, Ontario.

8 **FIELD AND LABORATORY VALIDATION OF A HIGH-VOL DENUDER FOR MINIMIZING PAH OXIDANT REACTIONS** 177
C.S. Davies[1], S. Guerin[1], J. Marr[2] and
M. Quilliam[2]. 1-Concord Scientific Corp.,
2-McMaster University, Ontario.

9 **A PARTICLE-SIZE SPECIFIC ELEMENTAL MASS BALANCE FOR APPORTIONMENT OF AMBIENT AEROSOL SAMPLED WITH MULTISTAGE FRACTIONATORS** 196
R.E. Jervis and T. Pringle, University of Toronto,
Toronto, Ontario.

45 **MUTAGENICITY OF COMPLEX MIXTURES OF PAHS' IN AMBIENT AIR PARTICULATE MATTER** 206
A.S. Raj and M. Katz, York University, Toronto,
Ontario.

46 **DOSE - RESPONSE STUDIES OF GASEOUS POLLUTANTS OF FOOD CROPS** 219
D.P. Ormrod and J. Petite, University of Guelph,
Guelph, Ontario.

47 **PRODUCTION OF OZONE INSENSITIVE WHITE BEAN VARIETIES** 242
T.E. Michaels, University of Guelph, Guelph,
Ontario.

48 **NICKEL CARBONYL AMBIENT MONITOR** 249
D.R. Hastie and H.I. Schiff, York University,
Toronto, Ontario.

49 **ELEMENTAL COMPOSITION OF AIR PARTICULATES INSIDE AND OUTSIDE A BUILDING** 263
P. Harvey, J.D. McArthur and G. Palmer,
Queen's University, Toronto, Ontario.

Paper No.		Page No.
50	**STUDY OF THE THERMAL REACTIONS OF PCDD ON FLYASH PARTICLES UNDER INCINERATOR CONDITIONS** ..... L.C. Dickson and F.W. Karasek, University of Waterloo, Waterloo, Ontario.	277
51	**CONTINUOUS EMISSION MONITORING FOR TOTAL HYDROCARBON AT SEWAGE SLUDGE INCINERATORS** .... J. Kosch, AMKO Systems Inc., Thornhill, Ontario.	305
52	**STUDY OF THE SPATIAL DISTRIBUTION OF THE IMPACT OF SUDBURY SMELTING EMISSIONS** .... E.A. McBean, J. Byrne, J. Donald and G. Farquhar, University of Waterloo, Waterloo, Ontario.	314
53	**CHARACTERIZATION OF BUILDING WAKE EFFECTS AT DARLINGTON NUCLEAR GENERATING STATION USING SULPHUR HEXAFLUORIDE AS A TRACER** .... G. Ogram[1], H. Sahota[2] and P.K. Misra[2]. 1-Ontario Hydro, 2-Environment Ontario.	330

PART B: WATER QUALITY RESEARCH

FEATURE PAPERS

A	**PREDICTIVE MODELS IN HAZARD ASSESSMENT OF GREAT LAKES CONTAMINANTS OF FISH** .... Dora R. May Passino: U.S. Fish and Wildlife Service, National Fisheries Centre - Great Lakes, Ann Arbor, Michigan, U.S.A.	1
B	**CONTROL OF TOXIC TRACE CONTAMINANTS IN MUNICIPAL WASTE WATER TREATMENT PLANTS** .... Henryk Melcer: Biological Processes Section, Wastewater Technology Centre, Canada Centre for Inland Waters, Environment Canada, Burlington, Ontario, Canada.	27

SESSION PAPERS

10	**TRACE ORGANIC CONTAMINANT REMOVAL FROM DRINKING WATER** .... J. Hilton, MacLaren Plansearch Inc., Toronto, Ontario.	52
11	**THE ROLE OF ORGANIC CARBON IN CONTROLLING THE OCCURRENCE OF DENITRIFICATION IN GROUNDWATER** ...... R.C. Starr and R.W. Gillham, University of Waterloo, Waterloo, Ontario.	67

Paper No. **Page No.**

12 **REPRODUCTIVE OUTCOMES IN SOUTHWESTERN ONTARIO, 1980 TO 1985** 82
J. McD. Robertson, H. Chan and I. Fyfe, University of Western Ontario, London, Ontario.

13 **ORGANIC CONTAMINANT STRUCTURE - PROPERTY - TOXICITY RELATIONSHIPS FOR AQUATIC ORGANISMS** 113
S. Abernethy and D. Mackay, University of Toronto, Toronto, Ontario.

14 **EFFECT OF LEAD, CADMIUM AND MERCURY ON THE TISSUE OF YOUNG FISH AND RATS: DEVELOPMENT OF BIOINDICATOR** 138
D.M. Nicholls, R. Angelow, K. Tiechert-Kuliszewska and G. Girgis, York Univesity, Toronto, Ontario.

15 **IN-SITU ASSESSMENT OF MIXED COPPER AND ZINC IMPACTS ON WHITE SUCKER (Castastomus Commersoni) POPULATIONS IN SEVERAL NORTHERN ONTARIO LAKES: AN EVALUATION OF THE ENVIRONMENTAL HEALTH APPROACH TO VALIDATING WATER QUALITY CRITERIA** 165
K.R. Munkittrick and D.G. Dixon, University of Waterloo, Waterloo, Ontario.

16 **THE FATE OF TOXIC ORGANIC CHEMICALS IN SEWAGE TREATMENT PLANTS** 176
B. Clark, S. Salenicks, J. Glynn Henry and D. MacKay, University of Toronto, Toronto, Ontario.

17 **TOXICITY OF PENTACHLOROPHENOL TO ZOOPLANKTON** 192
N.K. Kaushik and G. Stephenson, University of Guelph, Guelph, Ontario.

18 **DEVELOPMENT OF A STANDARD CLAM BIOMONITORING METHODOLOGY FOR THE DETECTION OF TRACE CONTAMINANTS WITHIN WATERS OF THE ONTARIO GREAT LAKES REGION** 205
A. Melkic, E. Greece and D. Lewis, Integrated Explorations Ltd., Guelph, Ontario.

54 **EVALUATION OF DATA ON THE EFFECTS OF HYDRAULIC CHARACTERISTICS AND EFFLUENT CHLORINATION ON THE INCIDENCE OF MICRO-ORGANISMS OF PUBLIC HEALTH SIGNIFICANCE IN RECEIVING WATERS** 219
M. Palmer, Gore & Storrie Ltd., Toronto, Ontario.

55 **LISTOWEL ARTIFICIAL MARSH TREATMENT PROJECT** 244
J. Herskowitz, S. Black and W. Lewandowski, Ministry of the Environment, Toronto, Ontario.

56 **A LOW PRESSURE HYDROCYCLONE FOR USE IN SEWAGE TREATMENT** 267
J.D. Boadway, Queen's University, Kingston, Ontario.

Paper No. Page No.

57 THE EFFECTS OF RURAL AND SUBURBAN DEVELOPMENT ON SURFACE WATER QUALITY IN FIVE SELECTED SUBWATERSHEDS ON THE UPPER HUMBER RIVER 294
B. Hindley, R. Hubbard and S. Maude, Metro Toronto Conservation Authority, Toronto, Ontario.

58 HUMBER RIVER/BLACK CREEK: DETAILED BACTERIOLOGICAL WATER QUALITY STUDY EXAMINING THEIR IMPACT OF SEDIMENT AND SURVIVAL TIMES 347
P.L. Seyfried and E. Harris, University of Toronto, Toronto, Ontario.

59 FEASIBILITY OF PLANT HARVESTING IN WATER QUALITY AMELIORATION AND PHOSPHORUS MANAGEMENT IN SHALLOW IMPOUNDMENT 392
P. McKee, K. Clarke-Whistler and G. Gaspardy, Beak Consultants Ltd., Toronto, Ontario.

60 TWO BIOASSAYS FOR THE RAPID DETERMINATION OF THE EFFECTS OF DREDGED SEDIMENT DISPOSAL IN PRIMARY PRODUCTION AND PHOSPHORUS KINETICS IN OPEN WATERS 415
C. Ewing and C. Nalewajko, University of Toronto, Scarborough, Ontario.

61 STOCHASTIC ESTIMATION OF AMBIENT WATER QUALITY IN THE THAMES RIVER 438
V.A. Graham, T.E. Unny and L. Logan, University of Waterloo, Waterloo, Ontario.

62 OTTAWA RIVER NUCLEAR SPILL CONTINGENCY MODEL DEVELOPMENT: PHASE II 467
T. Gowda, M. Palmer, C. Arnoldi and R. Jarvis, Gore & Storrie Ltd., Toronto, Ontario.

PART C: LIQUID & SOLID WASTE RESEARCH

FEATURE PAPERS

A HAZARDOUS WASTE DESTRUCTION: AN OVERVIEW OF APPROACHES AND SHORTCOMINGS 1
E. Timothy Oppelt: Thermal-Destruction Branch, Alternative Technologies Division, U.S.-EPA, Cincinnati, Ohio, U.S.A.

B AN OUTLINE OF U.S.-EPA RESEARCH ON LAND DISPOSAL OF HAZARDOUS WASTE 26
Norbert Schomaker: Hazardous Waste Engineering Research Lab., US-EPA, Cincinnati, Ohio, U.S.A.

Paper No. **Page No.**

SESSION PAPERS

19 **ASSESSMENT OF A PROTOTYPE SYSTEM FOR PYROLYSIS OF REFUSE DERIVED FUEL** 38
S.J. Thorndyke, Ontario Research Foundation, Mississauga, Ontario.

20 **MUNICIPAL SOLID WASTE FEASIBILITY OF GASIFICATION WITH PLASMA ARC** 63
G.W. Carter, Resorption Canada Ltd., Ottawa, Ontario.

21 **SEWAGE SLUDGE COMPOST AS TURF FERTILIZER** 78
J.L. Eggens, Ontario Agricultural College, University of Guelph, Guelph, Ontario.

22 **WASTE MANAGEMENT PLANNING FOR PHARMACEUTICAL INDUSTRY - PHASE I: INVENTORY AND DATA COLLECTION** 85
R. Makhija and R. Stairs, Tent University, Peterborough, Ontario.

23 **DEVELOPMENT OF GUIDELINES FOR THE UTILIZATION OF INDUSTRIAL WASTE IN BACKFILL AND CONSTRUCTION APPLICATIONS** 94
G. Zukovs, Canviro Consultants Ltd., Toronto, Ontario.

24 **NUMERICAL AND LABORATORY MODELLING OF TWO-PHASE FLOW IN POROUS MEDIA: 1 - TWO-PHASE GASEOUS FLOW, 2 - TWO-PHASE LIQUID FLOW** 117
G. Farquhar, E. McBean, J. Byrne, W. Abbott and R. Kell, University of Waterloo, Waterloo, Ontario.

25 **DEVELOPMENT OF POLYSULFIDE TECHNOLOGY FOR TREATMENT OF CONCENTRATED SPENT CYANIDE LIQUORS** ... 144
J.J. Gaczarczyk, University of Toronto, Toronto,

26 **TREATMENT OF LANDFILL LEACHATE BY SPRAY IRRIGATION** 175
R. McBridge, A.M. Gordon, P. Groenvelt, T. Bates and K. King, University of Guelph, Guelph, Ontario.

27 **CO-DISPOSAL OF INDUSTRIAL AND MUNICIPAL WASTES: PART II** 192
D. Kirk and M. Lau, University of Toronto, Toronto, Ontario.

63 **HAZARDOUS ORGANIC CHEMICALS IN GROUNDWATER AT ONTARIO LANDFILLS.** 206
J.F. Baker and J. Cherry, University of Waterloo, Waterloo, Ontario.

Paper No. **Page No.**

64 **DISPERSION OF THE STOUFFVILLE CONTAMINANT PLUME** 229
I. Proulx, R.N. Farvolden and E. Frind, University of Waterloo, Waterloo, Ontario.

65 **DEVELOPMENT OF DESIGN CRITERIA FOR OPTIMAL RECOVERY OF LEACHATE UNDER SANITARY LANDFILLS** 243
L. Arnaud, E. Frind, R. Farvolden and R. Gillham, University of Waterloo, Waterloo, Ontario.

66 **AN INVESTIGATION INTO THE REDOX CONDITIONS OF A LANDFILL LEACHATE PLUME CONTAINING VOLATILE ORGANICS, GLOUCESTER, ONTARIO** 272
L. Elliott, J. Develin, F. Michaels and W. Gorman, Queen's University, Kingston, Ontario.

67 **EFFECTS OF INCREASING AMOUNTS OF NON-POLAR ORGANIC LIQUIDS IN DOMESTIC WASTE LEACHATE ON THE HYDRAULIC CONDUCTIVITY OF CLAY LINERS IN SOUTHWESTERN ONTARIO** 294
R.M. Quigley and F. Fernandez, University of Western Ontario, London, Ontario.

68 **ASSESSMENT OF CONTAMINANT MIGRATION FROM INDUSTRIAL SOURCES DISCHARGING TO THE WELLAND RIVER** 315
M. Dickman, P. Hayes and I. Brindle, Brock University, St. Catherines, Ontario.

69 **EVALUATION OF CONTAMINANT VELOCITY GROUNDWATER IN LOW PERMEABILITY FRACTURE SHALE** 338
E. Sudicky, R. Blackport and J. Cherry, University of Waterloo, Waterloo, Ontario.

70 **GEOMECHANICAL INVESTIGATION OF NEAR-SURFACE FRACTURES IN CLAY TILLS** 349
M. Dusseault and A.Vorauer, University of Waterloo, Waterloo, Ontario.

71 **ORIGINS OF ELEVATED CHLORIDE CONCENTRATIONS IN GROUNDWATER SYSTEMS** 376
P.E. Pilon and K.W.F. Howard, University of Toronto, Scarborough, Ontario.

PART D: ANALYTICAL METHODS

FEATURE PAPERS

A **TRENDS IN MULTI-ELEMENT ANALYSIS: THE ROLE OF ICP-MS IN ENVIRONMENTAL APPLICATIONS** 1
Barry French, Institute for Aerospace Studies, University of Toronto, Toronto, Ontario, Canada.

Paper No. | Page No.

B DETECTION OF HYDROXYLATED NITRO-POLYNUCLEAR AROMATIC HYDROCARBONS AND KETONES IN AN AMBIENT AIR PARTICULATE EXTRACT USING BIOASSAY-DIRECTED FRACTIONATION 31
Marcia G. Nishioka and Corrine C. Howard, Analytical Chemistry Section, Battelle Columbus Division, Columbus, Ohio, and Joellen Lewtas, U.S. - EPA, North Carolina, U.S.A.

SESSION PAPERS

28 DIRECT SOLID SAMPLE ANALYSIS WITH THE DIRECT SAMPLE INSERTION DEVICE, PROMISE AND PROBLEMS 64
E. Salin and R.L. Sing, McGill University, Montreal, Quebec.

29 SCREENING METHODS FOR AIR AND WATER SAMPLES: APPLICATION OF INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP/MS) TO ELEMENTAL ANALYSIS 74
J. Van Loon and B.French, University of Toronto, Toronto, Ontario.

30 DEVELOPMENT OF SELENIUM ANALYSIS METHODOLOGY AT NG/L LEVELS FOR SOFT WATERS SUBJECT TO ACIDIC PRECIPITATION 97
L.M. Brown and J. Wehr, University of Western Ontario, London, Ontario.

31 EVALUATION AND OPTIMIZATION OF A TOC ANALYZER USING UV - PERSULPHATE DIGESTION 111
R.D. Evans, Trent University, Peterborough, Ontario.

32 DEVELOPMENT OF AN ULTRASONIC NEBULIZER FOR STABLE AND REPRODUCTIVE PRODUCTION OF AEROSOLS FOR ATOMIC SPECTROMETRIC ANALYSIS 112
J.C. Van Loon, University of Toronto, Toronto, Ontario.

33 DEVELOPMENT OF RECOMBINANT DNA PROBES TO DETERMINE THE ORIGIN OF FECAL STREPTOCOCCI AT THE TORONTO AREA BEACHES 133
W.C. Bradbury, M.A. Marko, L. Papageorgiou, D. Leight and D. Rego, University of Toronto, Toronto, Ontario.

34 PLANT BIOASSAYS FOR THE DETECTION OF ENVIRONMENTAL MUTAGENS 147
Wm. F. Grant, McGill University, Montréal, Quebéc.

35 A BIOLOGICAL INDICATOR SYSTEM TO IDENTIFY GENOTOXICITY OF IN-PLACE POLLUTANTS 167
D.R. Hart, J. Fichko, M. Brinkman and P. McKee, IEC Beak Consultants Ltd., Mississauga, Ontario.

Paper No.		Page No.
36	**FRESHWATER CLAMS AS MONITORS OF VARIATION IN ENVIRONMENTAL ACIDITY AND TRACE METAL LEVELS** ...... R.H. Green, S. Hinch and R. Bailey, University of Western Ontario, London, Ontario.	189
72	**ANALYSIS OF DIOXINS AND FURANS IN FISH AND OTHER BIOTA** .... F.W. Karasek, T. Thompson, D. Schelenberg and K. Naikwadi, University of Waterloo, Ontario.	215
73	**DEVELOPMENT OF COST-EFFECTIVE PROTOCOL FOR ROUTINE ANALYSIS FOR TRACE ORGANIC CONTAMINANTS IN MUNICIPAL WPCP RAW SEWAGE AND FINAL EFFLUENT** .... C. Chan[1], J. Martin[1], P. Pond[1], G. Rees[2], and T. Ho[2]. 1-Mann Testing Labs. Ltd., 2-Environment Ontario.	234
74	**APPLICATION OF GC HELIUM MICROWAVE PLASMA DETECTION TO THE RAPID SCREENING OF CHEMICAL WASTE** .... M. Danszinger, Barringer Magenta Ltd., Rexdale, Ontario.	255
75	**DEVELOPMENT OF METHODS SUITABLE FOR THE USE IN THE AMES SALMONELLA MUTAGENICITY ASSAY FOR THE COLLECTION OF ORGANICS PRESENT IN GROUNDWATER AND LANDFILL SITE MATRIX MAERIALS** .... G.H. Thomas, A. Horton and K. Matsummura, Ontario Research Foundation, Mississauga, Ontario.	271
76	**SYNTHESIS OF OXYGEN AND SULPHUR PAHS OF INTEREST IN ENVIRONMENTAL POLLUTION** .... E. Lee-Ruff and F. Ablenas, York University, Toronto, Ontario.	294
77	**DEVELOPMENT OF A ROBOTIC WORKSTATION FOR THE ROUTINE ANALYSIS OF ORGANICS IN BIOLOGICAL TISSUES USING ACID DIGESTION AND SOLVENT EXTRACTION METHOD** .... C. Chan[1], J. Martin[1], G.Ladwig[1], G. Rees[2], and G. Crawford[2]. 1-Mann Testing Labs Ltd., 2-Environment Ontario.	298
78	**SEPARATION AND IDENTIFICATION OF ORGANIC COMPOUNDS IN EXTRACTS OF AIR PARTICULATES BY HPLC AND GC/MS** .... K.P. Naikwadi, G. Charbonneau and F.W. Karasek, University of Waterloo, Waterloo, Ontario.	331

Paper No. **Page No.**

79 QUANTITATIVE DETERMINATION OF SELECTED PAHS' BY SHPOL'SKII AND JET-COOLED SPECTROSCOPY 355
C.M. Sadowski, J. Lai, H. Malle, S. Filseth and F. Morgan, York University, Toronto, Ontario.

80 NEW SYNTHETIC METHODOLOGY FOR THE EXPEDIENT PROVISION OF PURE PAH ANALYTICAL STANDARDS 384
V.A. Snieckus, University of Waterloo, Waterloo, Ontario.

PART E: ENVIRONMENTAL ECONOMICS

FEATURE PAPER

A THE ENVIRONMENT OF ECONOMICS - PAST PRESENT AND FUTURE ROLES OF ECONOMICS IN ENVIRONMENTAL MANAGEMENT 1
Clifford Russell, Director, Institute for Public Policy Studies, Vanderbilt University, Nashville, Tennesee, U.S.A.

SESSION PAPERS

37 ABATEMENT COST FUNCTIONS - THE WORKHORSE OF ENVIRONMENTAL MANAGEMENT 18
J. Donnan, C. Griffith, S. Glover and M. Dandele, Policy & Planning Branch, Ministry of the Environment, Toronto, Ontario.

38 MEASURING THE SOCIAL COSTS OF ELECTRICAL EXPORTS AND COST RECOVERY OPPORTUNITIES OF ENVIRONMENTAL PROTECTION OF ONTARIO HYDRO 39
W. Wianko and B. Green, Ontario Hydro, Toronto, Ontario.

39 QUÉBEC'S EXPERIENCE WITH THE ECONOMIC EVALUATION OF ENVIRONMENTAL REGULATIONS - WHAT LESSONS HAVE BEEN LEARNED 65
C. Sauvé, Ministére de l'Environment, Sainte-Foy, Québec.

40 3M'S POLLUTION PREVENTION PAYS PROGRAM 77
A.G. Mills, 3M Canada Inc., London, Ontario.

41 THE BENEFITS OF REDUCING LEAD IN U.S. DRINKING WATER 87
R. Levin, U.S.-EPA, Washington, D.C., U.S.A.

Paper No. **Page No.**

42 **ECONOMIC EFFECTS OF REDUCED FOREST GROWTH IN THE UNITED STATES' FOREST ECONOMY AND ON CANADIAN-U.S. LUMBER TRADE** 112
J.M. Callaway, Jr., Battelle Northwest Labs, Richland, Washington, U.S.A.

43 **SOME ECONOMICS OF THE GRAND CANAL** 129
A. Muller, Department of Economics, McMaster University, Hamilton, Ontario.

HAZARDOUS WASTE THERMAL DESTRUCTION:
AN OVERVIEW OF APPROACHES AND SHORTCOMINGS

By

E. Timothy Oppelt, Chief
Thermal Destruction Branch
Alternative Technologies Division
Hazardous Waste Engineering Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

Since 1980, the U.S. Environmental Protection Agency (EPA) has conducted extensive research to assess the performance of hazardous waste thermal destruction processes. This research has been designed to support the development and implementation of regulations and standards for controlling the safe operation of thermal destruction facilities in the United States. While these studies have largely shown thermal destruction to be the most practical and effective technology available for ultimate control of organic hazardous waste materials, some members of the scientific and environmental action community remain concerned about the long-term safety of the technology. The issues most frequently raised pertain to the possibility that harmful levels of heavy metals and incomplete combustion by-products may still be emitted from thermal destruction facilities that are otherwise meeting the current RCRA standards. The lack of available real-time monitoring techniques for tracking thermal destruction efficiency and detecting possible process upsets adds to the uncertainty and perceived risks associated with facility operation.

This paper will summarize the most recent data on thermal destruction facility performance with particular attention to metal and organic by-product emissions. Ongoing EPA research in this area and in real-time monitoring will be discussed. Real versus perceived concerns over thermal destruction will be put in perspective.

A PROFILE OF HAZARDOUS WASTE THERMAL DESTRUCTION: AN OVERVIEW OF APPROACHES AND SHORTCOMINGS

By

E. Timothy Oppelt
Chief, Thermal Destruction Branch
Hazardous Waste Engineering Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio

INTRODUCTION

Thermal destruction of hazardous waste involves the controlled exposure of waste to high temperature (usually 900°C or greater), and typically, an oxidizing environment. Thermal destruction processes include: thermal oxidation, starved air, or pyrolytic incineration systems; high temperature industrial processes such as boilers, cement kilns and industrial furnaces where hazardous waste is employed as a fuel; and various emerging processes which employ high temperatures, such as molten salt, plasma, or electric furnaces.

Properly designed and operated thermal destruction systems offer the prospect of destroying the hazardous organic components of waste streams while reducing waste volume and, in some instances, recovering energy or even materials such as hydrochloric or surfuric acid. Because of this, thermal destruction systems have emerged over the past decade as an increasingly desirable alternative to the more traditional hazardous waste disposal methods of landfilling, lagooning, and deep well injection.

However, improper design, operation, or use of such systems may also pose a threat to public health through emissions of potentially hazardous components of the waste or their combustion by-products. It was the recognition of the inherent environmental advantages of waste thermal destruction, balanced against the potential problems of improper practice that lead the U.S. Environmental Protection Agency (EPA) to develop performance standards and permit requirements for thermal destruction systems under the Resource Conservation and Recovery Act of 1976 (RCRA). Standards for incinerators have been in place since June 1982 (1) and standards are currently under development for disposal of hazardous wastes in industrial processes.

It is anticipated that thermal destruction will become even more important in the future as EPA responds to the Congressional mandate to restrict many hazardous wastes from land disposal and to effect corrective action at abandoned and uncontrolled disposal sites under the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA or "Superfund").

The objective of this paper is to summary current thermal destruction practice in the United States including process configurations, facilities, wastes typically handled, and process performance data. In addition, several of the new more important technical and "non-technical" issues concerning the use of thermal destruction over the long-term will be discussed. EPA research designed to resolve these issues will be outlined.

CURRENT PRACTICES

The most recent comprehensive data on hazardous waste thermal destruction practice come from EPA surveys of industry activity in 1981. It is estimated that the United States generated 264 million metric tonnes (MMT) that year, a large portion of which was predominantly non-hazardous materials (water) contaminated with smaller amounts of hazardous materials (2). Over 5.5 MMT was managed by thermal destruction, with 1.7 MMT disposed in 240 incineration facilities and 3.8 MMT disposed in over 1300 industrial boilers and other industrial furnaces. EPA estimates that as much as 25 MMT of the waste generated in 1981 could have been directly managed by thermal destruction (3).

Hazardous waste incineration practice is more extensively documented than is waste disposal in industrial boilers and furnaces. Incinerators have been the subject of EPA research for nearly a dozen years. Regulation, notification, and permit requirements have also produced a larger data base on incinerators. The practice of waste disposal as a fuel in industrial boilers and other industrial process furnaces will not be fully regulated until early 1987.

Table 1 profiles United States incineration practice in 1981 (4). The most commonly used design is the liquid injection incinerator. These units, which are most frequently employed for disposal of waste at the site of generation, are applicable almost exclusively for pumpable liquid waste. They are usually simple, refractory-lined cylinders (either horizontally or vertically oriented) equipped with one or more waste burners. Liquid wastes are injected through the burner(s), atomized to fine droplets, and burned in suspension. Auxillary fuel burners as well as separate waste injection nozzles may be oriented for axial, radial, or tangential firing.

Fixed hearth incinerators, which include both excess air, starved air or pyrolytic incinerators, are the second most utilized technology for hazardous waste incineration. The starved air type, first marketed in the early 1960's, have seen rapid growth in use, particularly for on-site disposal of solid wastes.

Starved air incinerators are typically two-stage combustion processes where liquid or solid waste is fed into a primary chamber operated at 50 to 80 percent of the stoichiometric air requirement. Vaporized and partially destroyed combustion products are then directed to an afterburner where excess air is added to complete the destruction, usually at higher temperature than that employed in the primary chamber.

Rotary kiln incinerators are the third most used incinerator design. They are the most versatile incinerators in the sense that they are applicable to the destruction of solid wastes, slurries, and containerized waste as well as liquids. Because of this, these units are most frequently incorporated into commercial off-site incineration facility designs. Waste is volatilized and partially destroyed in the rotating kiln, a cylindrical refractory-lined shell

TABLE 1

UNITED STATES HAZARDOUS WASTE INCINERATION PRACTICES (1981)

OWNERSHIP:	80% private 20% commercial and military
WASTE:	77% of facilities handle on-site wastes only 79% of units - liquids only 11% of units - bulk wastes (solids and liquids) 10% of units - special purpose
EQUIPMENT:	48% are liquid injection units 19% are fixed hearth units 6% are rotary kiln or combination units 27% are other (military, fluid bed, etc.) 45% have air pollution control systems 22% employ heat recovery
OPERATIONS:	median - 1800°F at 2 seconds residence time (gas) range - 1200°F - 2300°F 0.1 seconds - 6.5 seconds residence time most operate on an intermittent schedule
CAPACITY:	median - liquids, 150 gal/hr solids, 650 lb/hr range - 0.3 - 142 x 10^6 = Btu/hr
MANUFACTURING:	57 companies actively marketing incinerators 28 companies sold units most units installed since 1970 32-40 units under construction

mounted on a slight incline. Combustion gases then pass through a high temperature afterburner to complete the destruction process.

The typical air pollution control system employed on hazardous waste incinerators include combustion gas quench, venturi scrubber (for particulate control), acid gas adsorber for acid gas removal (packed bed or tray-tower type), and a mist eliminator. It is interesting to note, however, that more than half of the incinerators in 1981 employed no air pollution control system at all. Ostensibly this reflects that these facilities were handling low ash, low halogen content liquid waste streams for which such control measures are not typically necessary.

Precise information on the exact types of wastes going to thermal destruction facilities is difficult to obtain. Many facilities operate on an intermittent basis and handle mixtures of wastes which are difficult to describe in terms of EPA standard waste codes. A 1983 EPA study examined data on 413 waste streams going to 204 of the 240 incineration facilities in the United States (5). The major waste streams incinerated were spent non-halogenated solvents (EPA waste code F003) and corrosive and reactive wastes contaminated with organics (EPA waste codes D002 and D003). Together these accounted for 44 percent of the waste incinerated. Other prominent wastes included hydrocyanic acid (P063), acrylonitule bottoms (K011) and contaminated water (D001).

Hazardous waste materials are also being burned as fuels in a wide range of industrial applications. In 1981 these operations disposed of more than twice the amount of waste which was disposed via incinerators. Processes that have burned or do burn hazardous waste materials as fuels include: industrial boilers, cement kilns, iron-making furnaces, light weight aggregate and asphalt plants. The principal attractions to this approach include: fuel and waste transportation cost-savings, and waste disposal cost savings since hazardous waste used as a fuel can be sold.

The most recent source of information on waste fuel use in industrial processes was compiled for EPA in 1984 (6). The study synopsizes results of a national questionnaire of waste fuel and waste oil use in 1983. The study revealed that there were over 1,300 facilities using hazardous waste-derived fuels (HWDF), accounting for a total of 230 million gallons per year. The chemical industry (Standard Industrial Classification 28 [SIC]) accounted for 67 percent of this while operating only 12.4 percent of the facilities using HWDF. Other industries employing significant quantities of hazardous waste as fuel included: SICs 26 (paper), 29 (petroleum), 32 (stone, clay, glass, concrete), and 33 (primary metals). The majority (69 percent) of waste was burned in large quantities by a few facilities representing only a fraction (1.6 percent) of the 1300 facilities. These included medium- to large-sized industrial boilers, cement and aggregate kilns, and iron-making furnaces.

While waste-code-specific data on HWDF are not readily available, recent data indicate that of the HWDF burned in 1983, 30 percent was organic solvents, and 45 percent was other hazardous organics (6). Most of this waste was generated on-site and 74 percent of the balance arrived directly from an off-site generator rather than an intermediary.

PERFORMANCE OF THERMAL DESTRUCTION DEVICES

Since 1980, the U. S. Environmental Protection Agency (EPA) has conducted waste destruction performance tests at nearly 50 full-scale hazardous waste thermal destruction facilities in the United States. The facilities tested have included:

- ° commercial and on-site incinerators
- ° incineration ships
- ° cement kilns
- ° industrial boilers
- ° commercial boilers
- ° light weight aggregate kilns
- ° steel blast furnace
- ° batch asphalt plants

The principal objective of these tests has been to characterize stack emissions and residues to determine if these facilities are capable of meeting the waste destruction and control requirements of current EPA regulations and standards. In the case of hazardous waste destruction, the incineration standards promulgated under the Resource Conservation and Recovery Act of 1976 (RCRA) are the required performance level for incinerators or chosen (other thermal destruction processes performance benchmark (1). These standards require that facilities must demonstrate that they can attain:

(1) 99.99 percent destruction and removal efficiency (DRE) for each principal organic hazardous constituent (POHC) in the waste feed where:

$$DRE = (W_{in} - W_{out})/W_{in}) \times 100$$

Where: W_{in} = Mass feed rate of the principal organic hazardous constitutent (POHC) in the waste stream fed to the incinerator.

W_{out} = Mass emission rate of the POHC in the stack prior to release to the atmosphere.

(2) At least 99 percent removal of hydrogen chloride from the exhaust gas if hydrogen chloride stack emissions are greater than 1.8 kg/hr.

(3) Particulate matter emissions no greater than 180 mg/standard m^3 corrected to 7 percent oxygen in the stack gas. The measured particulate matter concentration is multipled by the following correction factor to obtain the corrected particulate matter emissions:

$$\text{Correction Factor} = 14/(21-Y)$$

Where: Y = measured oxygen concentration in the stack gas on a dry basis (expressed as a percentage).

The results of most of these performance tests have been compiled in published EPA reports and summarized in published papers (7-13). Tables 2, 3, and 4 describe the facilities and waste types encompassed by the test program and summarize waste destruction and emissions performance data. The data have shown that properly designed and operated incinerators, industrial boilers, cement kilns, and certain other industrial furnaces are capable of achieving or exceeding the RCRA DRE and hydrochloric acid gas requirements. The EPA also has conducted risk assessments using the emissions from the incinerators, boilers, and cement kilns tested. These assessments concluded that residual organic compounds in stack emissions posed no significant health risk (14-16).

TABLE 2

DESCRIPTION OF INCINERATION FACILITIES TESTED

FACILITY	CONTROL DEVICE	WASTE	DRE(a) (NO. OF NINES(b)	HCl CONTROL (AVERAGE)	AVERAGE PARTICULATE EMISSIONS (gr/dscf)
Commercial Rotary Kiln/ Liquid Incinerator (87 MM Btu/hr)	Packed Tower Adsorber Ionizing Wet Scrubber	Drummed, aqueous, liquid organic waste with carbon tetrachloride, TCE(c), perchloroethylene, toluene, phenol	5.3	99.4	0.67
Commercial Fixed Hearth, Two-Stage Incinerator (25 MM Btu/hr)	Electrified Gravel Bed Filter And Packed Tower Absorber	Liquid organic and aqueous waste with chloroform, carbon tetrachloride, TCE, toluene, perchloroethylene	4.4	98.3	.178
On-site Two-Stage Liquid Incinerator (6 MM Btu/hr)	Packed Tower Absorber	Liquid organic waste with carbon tetrachloride, dichlorobenzene, TCE, chlorobenzene, chloromethane aniline, phosgene	4.4	99.7	.027
Commercial Fixed Hearth, Two-Stage Incinerator (2 MM Btu/hr	None	Liquid organic waste with TCE, carbon tetrachloride, toluene, chlorobenzene	4.7	>4 lb/hr(d)	.089
On-Site Liquid Injection Incinerator (4.8 MM Btu/hr)	None	Liquid organic waste with aniline, diphenylamine, mono and dinitrobenzene	6.7	>4 lb/hr(d)	.092
Commercial Two-Stage Fixed Hearth Incinerator (10 MM Btu/hr)	None	Aqueous and organic liquid waste with carbon tetrachloride, TCE, benzene, phenol, perchloroethylene, toluene, methylethyl ketone	4.8	>4 lb/hr(d)	.40
On-site Rotary Kiln With/ Liquid Injection (35 MM Btu/hr)	Venturi Scrubber With Cyclone Separators And Packed Tower Absorbers	Liquid organic, point waste and filter cakes with methylene chloride, chloroform, benzl chloride, hexachloroethane, toluene, TCE, carbon tetrachloride	5.3	99.9	.01
Commercial Two-Stage Fixed Hearth Incinerator (75 MM Btu/hr	Venturi Scrubber	Aqueous and organic liquids and solid waste with methylene chloride, chloroform, carbon tetrachloride, hexachlorocylopendtadiene, toluene, benzene, TCE	4.6	98.3	.075

(a) Destruction and Removal Efficiency (Mass Weighted Average For All POHCs >100 ppm In Waste Feed)
(b) For Example, 99.995 Percent DRE = 4.5 nines
(c) TCE = Trichloroethylene
(d) No HCl Control Device, Waste Low In Total Organic Chlorine Content

TABLE 3

DESCRIPTION OF INDUSTRIAL BOILER FACILITIES TESTED

FACILITY	CONTROL DEVICE	WASTE	DRE(a) NUMBER OF NINE(b)
(1) Watertube Stoker - wood-fired (10 MMBtu/Hr)	Multiclone	Creosote Sludge With Phenol Pentachlorpheno And Napthalene	3.8
(2) Packaged Firetube - gas-fired (8.5 MMBtu/Hr)	None	Alkyd Wastewater With Toluene	4.1
(3) Field Erected Watertube - gas/oil-fired (230 MMBtu/Hr)	None	Phenol Waste	5.6
(4) Converted Stoker - oil-fired (90 MMBtu/Hr)	None	Methanol, Toluene And Chlorinated Organics Including Perchloroethylene	4.8
(5) Packaged Watertube - oil-fired (110 MMBtu/Hr)	None	Methyl Methacrylate By-products With Carbon Tetrachloride, Chlorobenzene And TCE(c)	4.5
(6) Converted Watertube - oil-fired (60 MMBtu/Hr)	None	Paint Solvents With Carbon Tetrachloride, TCE, Toluene And Chlorobenzene	3.8
7) Modified Firetube - waste-fired (40 MMBtu/Hr)	2 Scrubbers In Series	Highly Chlorinated Organics Including Carbon Tetrachloride	4.8
8) Tangentially Fired Watertube - coal-fired (250 MMBtu/Hr)	ESP	Methyl Acetate, Carbon Tetrachloride, Trichloroethane Chlorobenzene	4.1
9) Packaged Watertube - gas-fired (62 MMBtu/Hr)	None	Aniline Waste With Nitrobenzene, Carbon Tetrachloride, TCE, Benzene, Toluene	4.8
10) Packaged Firetube - waste-fired (10 MMBtu/Hr)	None	Toluene, Chlorinated Organics, Including Carbon Tetrachloride, TCE	5.0
11) Packaged Watertube - oil-fired (60 MMBtu/Hr)	None	Blended Waste With Light Oil And Carbon Tetrachloride, Benzene, TCE, Toluene	5.7

a) Destruction And Removal Efficiency (DRE), Mass Weighted Average of POHCs >100 ppm in Waste Feed

b) For Example, 99.995 Percent DRE = 4.5 Nines

c) TCE = Trichloroethylene

TABLE 4

DESCRIPTION OF INDUSTRIAL KILNS FACILITIES TESTED

FACILITY	CONTROL DEVICE	WASTE	DRE[a] NUMBER OF NINES)[b]
(1) Wet Process Cement Kiln Non-atomized Waste 140 MMBtu/Hr - oil fired	Fabric Filter	Waste Liquids Including, Methylene Chloride, Chloroform, Carbon Tetrachloride	2.8
(2) Wet Process Cement Kiln Atomized Waste 170 MMBtu/Hr - coal fired	ESP	Waste Liquids, Including Methylene Chloride, MEK, Trichloroethane, Toluene, Freon 113	4.2
(3) Dry Process Cement Kiln Non-atomized Waste 228 MMBtu/Hr - coal/coke fired	ESP	Waste Liquids, Including Methylene Chloride, Freon 113, MEK, Toluene, Trichloroethane	4.1
(4) Dry Process Cement Kiln Atomized Waste 300 MMBtu/Hr - coal/coke fired	Fabric Filter	Waste Liquids, Including Trichloroethane Trimethylbenzene, Xylene, Methylene Chloride	>4
(5) Lime Kiln Atomized Waste 50 MMBtu/Hr - coke/gas fired	Fabric Filter	Waste Liquids, Including Methylene Chloride, MEK, Trichloroethylene	4.7
(6) Shale Aggregate Kiln Atomized Waste 35 MMBtu/Hr - coal fired	Scrubber	Waste Liquids, Including Perchloroethylene, Methylethyl	>5
(7) Clay Aggregate Kiln 20 MMBtu/Hr - coal fired	Scrubbers	Waste Liquids, Including Methylethyl Ketone, Perchloroethylene And Toluene	4.8
(8) Clay Products Kiln Atomized Waste 37.5 MMBtu/Hr - oil fired	Fabric Filter	Waste Liquids, Waste Oil, Freon 113. Perchloroethylene Carbon Tetrachloride, Benzene, TCE, Toluene	3.5

(a)Destruction And Removal Efficiency (DRE), Numerical Average Of Major POHCs
(b)For Example, 99.995 Percent DRE = 4.5 Nines
(c)MEK = Methyethyl Ketone

Remaining Issues

While thermal destruction represents the most effective and widely applicable control technology available today for organic hazardous waste, a number of issues remain concerning its use in the long term. These include:

- ° Destruction effectiveness on untested/unique wastes
- ° Detection of process failure
- ° Control of heavy metal emissions
- ° Emissions of combustion by-products
- ° Available thermal destruction capacity
- ° Permits and public acceptance

The balance of this paper will attempt to define each of these issues more fully, present applicable data and other information to put these concerns into some perspective, and summarize ongoing EPA research designed to improve our understanding in these areas.

Untested Wastes

All of the performance data which have been used in the development and assessment of thermal destruction regulations and standards have obviously been collected for waste/thermal-technology combinations typical of current practice. However, the character of wastes which may be subjected to incineration in the near future will begin to change, perhaps dramatically. These changes will be influenced by EPA action to restrict many wastes from land disposal under the Hazardous and Solid Waste Act Amendments of 1984 (HSWA) and by increased emphasis upon remedial action at "Superfund" sites. Incineration will emerge as a feasible technological alternative for destruction of many of these wastes and site clean-up residues. However, EPA and industry will have considerably less experience in handling these wastes. They will tend to have higher solids and water content, be more complex in their physical and chemical composition, have lower heat content, and potentially contain higher levels of hazardous metals and high hazard organics compared to wastes which are typically incinerated today.

Consequently, while incineration is capable of achieving high levels of destruction for today's wastes, future wastes may place new performance demands on current technology. For instance, 99.9999 percent DRE is now required for wastes bearing chlorinated dioxin and furan compounds. Many of these wastes appear at Superfund sites. EPA is also studying the need for heavy metals control regulations for incinerators. That effort may suggest the need for improved air pollution control systems or waste pretreatment. Thus, performance testing of incinerators and other thermal destruction devices must continue in order to assure destruction and removal effectiveness for these untested wastes, to assess process limitations and waste pretreatment requirements, determine the safety of process residues, and to improve our ability to predict performance on new waste materials.

Detection Of Process Failure

While well-operated thermal destruction facilities achieve high levels of organic hazardous material destruction, little is known about the impact of process upsets or failure modes upon emissions. This is often a concern of the public in hearings and permit actions.

While convincing trial burn performance data can be presented, uncertainty and distrust may exist regarding the reliability of thermal destruction systems in day-to-day operation after a permit is approved and when regulators are not present.

Currently, permit conditions are primarily based upon process operating conditions which are documented during the conduct of a successful trial burn; i.e., one which demonstrated that the facility achieved or exceeded the RCRA performance standards. Operating conditions (e.g., combustion temperature, O_2, and CO in stack emissions, etc.) must be used as surrogates for similar high performance after the fact since there is currently no real-time method to determine DRE for specific POHCs. DRE can only be determined with certainty via expensive, often multi-day testing procedures. Analysis results may take weeks or months to complete. While EPA believes this approach is reasonable and protective of public health and the environment, many argue that the availability of a real-time monitoring technique to detect process upsets and alert operators to automatically take corrective action would significantly increase public acceptance of thermal destruction technology.

EPA is currently conducting extensive research to assess the impact of the most likely process failure modes upon performance. The failure conditions being studied include: improper waste atomization; overfeeding or unstable feeding of waste; inadequate combustion temperature; post-combustion quenching of destruction reactions; inadequate combustion mixing; and a variety of other process-specific variables. This research is being conducted in laboratory- and pilot-scale incineration systems at EPA facilities in Cincinnati, Ohio, Research Triangle Park, North Carolina, and Jefferson, Arkansas. The experimentation is attempting to correlate process failure with a variety of potential performance indicators which can be inexpensively measured more or less instantaneously. The indicators currently being examined include: total unburned hydrocarbon emissions (TUHC); carbon monoxide emissions (CO); oxygen levels in stack emissions (O_2); and emissions of tracer compounds such as sulfur hexafluoride and various freons which could be added to a waste stream and be monitored as a potential surrogate for other organic compound destruction.

Results to date have not conclusively shown a universal correlation of any of the performance indicators with DRE. It appears that such correlations may be very waste and facility specific. TUHC and CO emissions appear to hold the most promise. As the research progresses, EPA hopes that statistical and engineering analysis will reveal a reliable approach which could be used during the trial burn to calibrate individual facilities for a DRE/surrogate relationship. The appropriate monitor could then be used for process control or compliance monitoring during normal operation.

Metal Emissions

Metals such as arsenic, barium, berylluim, chromium, lead, mercury, nickel, and zinc are of possible concern in waste incineration because of their presence in many hazardous wastes and because of possible adverse health effects from human exposure to emissions. Incineration will change the form but not the content of metal fractions in waste streams. As a result, metals are expected to emerge from the combustion zone essentially in the same total quantity as the input. The principal environmental control concern therefore centers around where and in what physical or chemical form the metals partition in the combustion system, i.e., bottom ash, fly ash, in APCD residues, or stack emissions.

The primary controller for metals emissions from incineration is the RCRA particulate emission standard of 180 mg/dry standard cubic meter. Half of the incinerators evaluated in EPA's incinerator testing program (4 of 8) failed to meet this standard. Two of the facilities which failed did not have particulate pollution control systems. The other two units employed somewhat dated and poorly-maintained systems. Similar results are also being observed in trial burn data being submitted to EPA in permit applications.

Data were collected on actual metal emissions during the EPA incinerator testing program, as well as during certain of the other facility tests (cement kilns, waste oil combustion, boilers). As part of EPA's Regulatory Impact Assessment performed to examine the impact of the regulations on the regulated community and to examine the health and environmental effects of the regulation, the risks due to emissions of principal organic hazardous constituents (POHCs), combustion by-products (PICs), and metals were developed and presented for incinerators (14). The overall summary of results is presented in Table 5.

TABLE 5. Total excess lifetime cancer risk to the maximum exposed individual for incinerator emissions

POHCs	10^{-7} to 10^{-10}
PICs	10^{-7} to 10^{-11}
Metals	10^{-8} to 10^{-5}
TOTAL	10^{-8} to 10^{-5}

The risks from metals emissions ranged from two to six orders of magnitude higher to one order of magnitude lower than from POHCs and PICs, and dominated the total risk values.

The risk estimates for metals were based on emission measurements from the stack sampling program conducted during the tests. The metals analyses were conducted on the particulates collected during stack sampling. The risk analysis for metals was conducted in two parts; for metals exhibiting carcinogenic properties, and for non-carcinogenic effects (threshold) for a range of metals.

While these results show that the health risks of most wastes in most incinerators are low, risks from metal emissions show the greatest potential for exceeding a 10^{-6} cancer risk. This is particularly true for facilities which may be operating at or near the RCRA particulate emission standard or those which may wish to incinerate waste higher in metal content in the future.

EPA is considering various regulatory options for controlling metal emissions from hazardous waste thermal destruction facilities. To support the development of these potential regulations, research is underway to assess the character and fate of metals in incineration systems as a function of incinerator design and operation, waste characteristics and air pollution control system operation. Testing in pilot-scale incinerators will be conducted at EPA's Combustion Research Facility in Jefferson, Arkansas to develop metal partitioning models for conventional incineration system configurations. These models will be verified in field tests of commercial systems. The waste impact of pretreatment or improved air pollution control systems will be assessed in the research program.

Combustion By-Product Emissions

The current RCRA incineration standards regulate destruction and removal only for the major hazardous compounds in the waste. One of the concerns expressed by scientists and environmentalists regarding hazardous waste thermal destruction is the possible impact on human health and the environment of emissions of potentially hazardous products of incomplete combustion or PICs. This concern prevails in spite of the fact that EPA assessments have indicated that the risks from PIC emissions are low. In case of incinerators, Table I shows that the total excess lifetime cancer risk to the maximum exposed individual are essentially the same for PICs and POHCs, and both are less than 10^{-7}. Analysis of emissions data from tests of hazardous waste destruction in industrial boilers revealed that risks from PICs were consistently higher than POHC emission risks, but that neither risk was ever greater than 10^{-6} (16).

One basic issue which remains unresolved is the definition of a PIC. While a POHC is defined in the RCRA regulations, a PIC is not in a rigorous sense. Thus, there is often confusion even among scientists working in the area. Strictly speaking, PICs are organic compounds which are present in the emissions from the combustion process, which were not present or detectable in the fuel or air fed to the combustor. In EPA's test program, compounds were considered to be PICs if they were regulated organic compounds (i.e., listed in Appendix VIII of CFR 40 Part 261) which were detected in stack emissions, but not present in the waste feed at concentrations greater than 100 ppm.

Compounds in the emission stream which are identified as PICs can actually be any one of the following:

1. Compounds resulting from the incomplete burning of the principal organic hazardous constituents (POHCs), i.e., fragments of the original POHCs.

2. New compounds "created" in the combustion zone and downstream as the result of partial destruction followed by recombination with other compounds or fragments present.

3. A compound originally present in the feed stream before combustion but not specifically identified as a POHC.

EPA field studies of thermal destruction systems have identified 55 Appendix VIII compounds (28 volatile and 27 semi-volatile) in stack emissions (7,8,11). These compounds were emitted at rates that span over five orders of magnitude, 0.09 to 13,000 nanograms of emissions per kilojoule of combustor heat input [ng/kJ]. The volatile compounds tended to be detected more often and in significantly higher concentrations than the semivolatile compounds. The compounds that occurred most frequently and in the highest concentrations, nine volatile and six semivolatile, are listed in Table 6.

In a recent study (18), a subset of the available data was defined which consisted of only those data where specific compounds were identified in stack emissions but not in the waste burned (i.e., PICs). These data were used to compare emissions from incinerators, boilers, and kilns as shown in Table 7. Three of the semivolatile compounds listed earlier were not included because there was minimal data for comparison. The data in Table 7 show that values from test run to test run varied considerably, thus these data do not allow prediction levels for all three combustion devices. Many of the volatile compounds showed higher levels for boilers, and incinerators tended to show higher levels for semivolatiles.

TABLE 6. Most frequent thermal destruct process stack emissions

VOLATILE COMPOUNDS	SEMI-VOLATILE COMPOUNDS
Benzene	Naphthalene
Toluene	Phenol
Carbon tetrachloride	Bis(2-ethylhexy)phthalate
Chloroform	Diethylphthalate
Methylene chloride	Butylbenzylphthalate
Trichloroethylene	Dibutylphthalate
Tetrachloroethylene	
1,1,1-Trichloroethane	
Chlorobenzene	

Data were also available from several baseline (no waste firing) tests on boilers and kilns. The fuel for most of the baseline tests was oil or natural gas, with some coal burned in a few kiln tests. These data were used to compare emissions from hazardous waste combustion with combustion of fuel without hazardous waste. Table 8 presents this comparison for volatile compounds. Sufficient data were not available for a similar comparison for semi-volatile compounds. Considering the wide range in values from test to test, the data

TABLE 7. Emission rates of specific compounds from incinerators, boilers, and kilns, ng/kJ

	Incinerators		Boilers		Kilns	
	Mean	Range	Mean	Range	Mean	Range
Benzene	87	2-980	30	0-300	580	290-1,000
Toluene	1.6	1.5-4.1	280	0-1,200	----	No data ----
Carbon tetrachloride	0.8	0.3-1.5	1.8	0-7.2	----	No data ----
Chloroform	3.8	0.5-8.4	120	0-1,700	----	No data ----
Methylene chloride	2.2	0-9.6	180	0-5,800	----	No data ----
Trichloroethylene	5.2	2.3-9.1	1.2	0-13	1.3	0.7-2.8
Tetrachloroethylene	0.3	0-1.3	63	0-780	----	No data ----
1,1,1-Trichloroethane	0.3	0-1.3	7.5	0-66	2.4	(One value)
Chlorobenzene	1.2	0-6.0	63	0-1,000	152	33-270
Naphthalene	44	0.7-150	0.6	0.3-2.1	----	No data ----
Phenol	7.8	0-16	0.3	0-0.8	0.02	0-0.05
Diethylphthalate	3.7	2.8-4.8	0.4	0.04-1.6	----	No data ----

in Table 8 suggest there is little inherent difference between waste and fuel combustion in emissions of the volatile compounds shown in the Table.

Sufficient data for five semivolatile compounds were available to compare their emissions when burning hazardous waste versus their emissions from municipal incinerators and coal-fired power plants. Similar data were not available for volatile compounds. Table 9 presents this comparison. The four phthalate compounds in the Table all show very similar emission rates from all three sources. Naphthalene emissions were lower for power plants then the other two sources. Again, the data suggests that for some compounds there is little inherent difference between combustion sources.

An additional concern many have expressed regarding the issue of PICs is that EPA risk assessments have been limited to only metals and the Appendix VIII organic compounds. Comparison of total hydrocarbon emissions with the total quantity of organic compounds emitted has revealed that only a relatively small percentage of the total hydrocarbon emissions have been identified (Table

TABLE 8. Volatile compound emission rates from hazardous waste and fuel combustion, ng/kJ

	Waste		Fuel	
	Mean	Range	Mean	Range
Benzene	120	0-1,000	320	0-1,100
Toluene	210	0-1,200	190	0-1,500
Chloroform	90	0-1,700	14	0-800
Methylene chloride	130	0-5,800	160	0-3,400
Trichloroethylene	1.8	0-13	1.5	0-14
Tetrachloroethylene	49	0-780	7.7	0-52
1,1,1-Trichloroethane	5.6	0-66	1.7	0-14

10). This has raised the question of what other potentially hazardous compounds (Appendix VIII or non-Appendix VIII) might remain in the unidentified emissions and what additional risk these might pose.

EPA has had some of the incinerator test analyses reviewed to identify additional compounds (18). This review showed that the quantity of volatile non-Appendix VIII compounds detected by GC/MS varied from only a fraction of the total quantity of Appendix VIII compounds in one case to twice the quantity in another case. For semi-volatiles, the search showed that the total of non-Appendix VIII compounds was 3 to 30 times the quantity of Appendix VIII compounds. Some of the non-Appendix VIII compounds identified in the highest concentrations were:

Acetone
Acetophenone
Benzaldehyde
Benzenedicarboxaldehyde
Benzoic acid
Chlorocyclohexanol
Cyclohexane
Cyclohexanol
Cyclohexene
Dioctyl adipate
Ethenylethylbenzene
Ethylbenzaldehyde
Ethylbenzene
Ethylbenzoic acid
Ethylphenol
(Ethylphenyl)ethanone
Ethenylbenzene
Phenylacetylene
Phenylbutenone
1,1'-(1,4-Phenylene)-bisethanone
Phenypropenol
Propenylmethylbenzene
Tetramethyloxirane
Trimethylhexane

TABLE 9. Semi-volatile compound emission rates from hazardous waste combustion, municipal incinerators, and coal power plants, ng/kJ

	Hazardous waste		Municipal waste		Coal power plant	
	Mean	Range	Mean	Range	Mean	Range
Naphthalene	17	0.3-150	71	0.4-400	0.5	0.06-1.8
Bis(2-ethylhexyl)phthalate	4.6	0-21	4.6	0.4-12	7.6	0.2-24
Diethylphthalate	1.2	0.04-4.8	0.5	0.0.9	2.8	0.4-5.7
Butylbenzyphthalate	3.7	0.7-23	-- No data ----		0.5	0.3-1.0
Dibutylphthalate	0.3	0-1.1	3.9	1.5-7.6	3.0	0.09-8.7

TABLE 10. Total appendix VIII compounds measured as percent of total hydrocarbon

	Mean	Range
Incinerators	12	0.3-44
Boilers	0.4	0.01-1.1
Kilns	14	0.1-50

The EPA Science Advisory Board has reviewed the available emissions data for incinerators. While they have concluded that incineration is an effective destruction technology, they also concluded that a complete risk analysis was limited by an incomplete knowledge of the full range of compounds which are emitted from the stack during thermal destruction of hazardous waste (19). To address this issue, EPA will conduct an emissions test at a full-scale hazardous waste incinerator in the Fall of 1986 in an effort to quantify total mass emissions (TME). The project will employ a broader array of sampling and analysis techniques than used in previous testing. The difference between steady-state operation and operation with typical transient conditions will also be studied. It is hoped that this test will characterize emissions sufficiently to allow a complete risk assessment and verify previous conclusions on risks.

Capacity

There has been considerable discussion recently regarding the need for increased hazardous waste thermal destruction capacity in the United States.

This issue is important for two reasons. First, thermal destruction is being identified by EPA as best demonstrated available technology for many of the wastes which will be restricted from land disposal under HSWA. The dates when restrictions on specific waste streams become effective will be, in part, a function of the availability of permitted thermal destruction capacity to handle the amount of waste expected to be diverted from land disposal.

Capacity is also an issue in the issuance of permits to incinerate hazardous wastes at sea in specially-designed incineration ships. Approval of disposal at sea is, in part, dependent upon successfully demonstrating a sufficient need to do so (i.e., insufficient land-based capacity).

EPA has conducted several studies of thermal destruction capacity over the past several years (17,20,21). The most recent data on incinerator capacity is summarized in Table 11. There are 208 operating incinerator facilities in the United States. Of these, 34 have final operating permits and 174 have filed final applications which are being evaluated. Design capacities were obtained for 87 percent of the 208 units. The design, or nameplate, capacity of these reporting units is 6.28 billion Btu/hr. Extrapolating this statistic to include all 208 incinerators subject to the RCRA regulatory program, the national capacity could be 7.2 billion Btu/hr, which is equivalent to approximately three (3) million metric tonnes of hazardous waste per year. Fume incinerators which are incinerating liquid hazardous waste appear to be approaching their capacity (94 percent), followed by rotary kiln incinerators (77 percent).

TABLE 11. Estimation of available hazardous waste incinerator capacity by incinerator design

INCINERATOR DESIGN	NUMBER OF UNITS	AVERAGE DESIGN CAPACITY (Million Btu/hr)	UTILIZATION (Percent)	AVAILABLE CAPACITY (Million Btu/hr)	PERCENT WITH AIR POLLUTION CONTROL EQUIPMENT
Rotary Kiln	42	58.7	77	570	90
Liquid Injection	95	36.1	55	1540	42
Fume	25	29.5	94	40	40
Hearth	32	22.5	62	270	38
Other	14	23.8	--	110	--
Total or Average Values	208	37.6*	67**	2530	50

*181 incinerators reporting
** 90 incinerators reporting

The study also revealed that since 1981, almost 100 incinerators had withdrawn from the RCRA system because they either ceased operation or were no longer handling hazardous wastes. Also, of the 57 companies identified as marketing hazardous waste incinerators in 1981, 23 have either gone out of business, left the hazardous waste incinerator business, or put considerably less emphasis on this activity. Only one new company is pursuing this market. Apparently, many of the companies that were anticipating large growth in the incineration market in 1981 have abandoned the business as a result of selling only a few or no units since then. The remaining 35 manufacturers, however, reported that 111 new incinerators had been sold since 1981.

It is believed that 12 cement kilns have received the hazardous waste storage permits necessary to burn hazardous waste as a fuel in their processes (22). This corresponds to a capacity of between 87,000 tonnes of waste per year. These estimates are one to four percent of the estimated potential cement kiln capacity. The available capacity estimates for wastes that could be destroyed in cement kilns range from two (2) to six (6) million tonnes per year, or from 0.8 to 2.3 percent of the hazardous waste generated annually in the United States.

There are also over 43,000 industrial boilers in the United States of sizes and designs which are potentially able to achieve acceptable waste destruction.[7] Of this population, 5,500 boilers are located in the chemicals, petroleum refining, and paper industries. These boilers are accessible to about 70 percent of total hazardous waste generated and over 95 percent of all potentially combustible hazardous waste, and are the most likely boiler candidates for waste firing. EPA estimates that approximately 1300 boilers are actually disposing of 3.5 million tonnes of hazardous waste annually (13). If the remaining 4,200 boilers in the chemicals industry were to begin using hazardous waste as fuel at an equivalent rate, this quantity could increase to 14.8 million tonnes/year.

The conclusion one draws from these data is that, in the very near term, there appears to be sufficient thermal destruction capacity in the United States (Table 12). In addition, if permits are granted for the two Vulcanus seabased incinerators, incineration capacity for liquid wastes could increase by 100,000 tonnes per year.

EPA has estimated the amount of hazardous waste which might be redirected to commercial incineration as a result of restrictions upon disposal in landfills, lagoons, and injection wells (21). Each of these three restriction scenarios are projected to result in an excess of commercial incineration demand over existing capacity of 215 to 306 percent for liquid wastes alone. Translated into facilities, this converts to as many as 26 incinerators (20,000 tonnes each). Solid hazardous waste and Superfund clean-up residues would further increase the shortfall.

While there are many boiler and kiln facilities which could dispose of waste, much of the waste which will become available for use in these thermal destruction facilities in the future is likely to be increasingly less attractive to them. This waste will tend to be much less combustible and higher in solids, ash, and water content and, therefore, more suited to more conventional commercial incineration facilities. Thus, unless the rate of commercial incineration

TABLE 12. United States thermal destruction capacity for hazardous waste (million tonnes per year)

Facility Type	Current Utilization	Capacity	% Utilization
Incinerators (land-based)	1.7	2.7	63
Industrial Boilers	3.5	14.8	24
Cement Kilns	0.9	2-6	15-45
Incinerators (ocean)	0	0.1	0

facility permitting and construction increases (particularly for solid hazardous wastes) the effective capacity may well be insufficient for new wastes which will enter the system from land disposal restriction and Superfund clean-up activities.

Permits And Public Acceptance

While thermal destruction offers many advantages over existing hazardous waste disposal practices and may help to meet the anticipated need for increased waste management capacity, public opposition to the permitting of new thermal destruction operations has been strong in recent years. The normal time required for permitting new incineration facilities is three years. This time as well as the expense of obtaining a permit may be greatly increased if public opposition exists.

The amount of public opposition to proposed permits for land-based incinerator facilities varies by location and type of waste. On-site facilities that directly serve a single waste generator have greater public acceptance than off-site commercial incinerators that serve multiple generators in a large market area. Off-site facilities are often not perceived as providing sufficient economic benefits to the local community to offset the risks associated with the importation of wastes from other areas. On-site facilities are more clearly perceived as being linked to businesses that are important to the local economy, and are generally not perceived as being importers of hazardous waste. Opposition has tended to focus primarily on new off-site facilities, including incinerator ships, and on new applications to burn PCBs, which critics view as particularly hazardous.

In an effort to assess the dilemma of perceived benefits versus public concerns, EPA conducted an assessment in 1985 to determine if there was a need for a change in the Agency's approach toward regulating thermal destruction (23). The major concerns reported by citizens included:

- Hazardous material spills in storage, treatment, and handling.
- Environmental and health impacts of land-based and ocean facilities.
- Poor site selection processes.
- Distrust of incinerator owners and operators.
- Inability of government agencies to enforce compliance.

The study concluded that public opposition to both land and ocean incineration may decline somewhat if EPA addresses more fully some citizen concerns regarding national regulatory strategy, local community impacts, equity of facility siting, public decision-making processes, and especially enforcement plans and capacity. There is a need to better communicate how health and environmental concerns and priorities are reflected in the Agency's regulations and standards. Better communication of EPA's overall regulatory policy, strategy, and activities for decisions on proposed permits for individual incinerator facilities or vessels is needed. Better public communication is also important for improving EPA's credibility with the public, which is a necessary foundation for the effective accomplishment of the Agency's mission.

CONCLUSIONS

Thermal destruction of hazardous waste in incinerators and certain industrial processes represents the most effective technique currently available for organic wastes. While current assessments reveal that the emissions of metals and hazardous organics from these facilities present no significant health risks, a variety of scientific and public concerns remain over their safety. EPA is striving to improve our understanding of thermal destruction through a full range of ongoing research designed to answer the remaining concerns and bolster public confidence in thermal destruction. This research includes investigations into the development of real-time indicators of incinerator performance, performance tests on untested and high hazard wastes streams, and assessments of the impact of thermal destruction process upsets on emissions of metals and incomplete combustion by-products.

REFERENCES

1. Federal Register, Vol. 47, No. 122, pg 27516-27535, June 14, 1982, 40 CFR Parts 122 and 264.

2. National Survey of Hazardous Waste Generators and Treatment, Storage and Disposal Facilities Regulated Under RCRA in 1981, U.S. EPA, 1984 (Available from U.S. Government Printing Office, Washington 20402, $9.50, Order No. 055000-00239-8).

3. Draft Regulatory Analysis for Proposed RCRA Regulations on Burning of Hazardous Wastes, U.S. EPA, January 1984.

4. A Profile of Existing Hazardous Waste Incineration Facilities and Manufacturers in the United States, U.S. EPA, February 1984 (Available from National Technical Information Service [NTIS], Springfield, VA, 22161, Order No. PB-84-157072).

5. Composition of Hazardous Waste Streams Currently Incinerated, Vogel, et al., Mitre Corp., U.S. EPA, April 1983.

6. Used or Waste Oil and Waste Derived Fuel Material Burner Questionnaire for 1983, Westat, Inc. for U.S. EPA, 1984.

7. Performance Evaluation of Full-Scale Hazardous Waste Incineration (5 Volumes, U.S. EPA, November 1984. (Available from NTIS, Order No. PB-85-129500).

8. Engineering Assessment Report - Hazardous Waste Co-Firing in Industrial Boilers (2 Volumes), U.S. EPA, June 1984 (Available from NTIS, Order No. PB-85-197838/A05 and A08).

9. Destroying Chemical Wastes in Commercial-Scale Incinerators, U.S. EPA, 1977.

10. Evaluation of Hazardous Waste Incineration in Aggregate Kilns; Florida Solite Corp., U.S. EPA, May 1985 (Available from NTIS, Order No. PB-85189/066AS).

11. "Hazardous Waste Incineration in Industrial Processes: Cement and Lime Kiln," R. E. Mournighan, et al., Proceedings, International Conference on New Frontiers for Hazardous Waste Management, U.S. EPA Report No. 600/9-885/025, September 1985.

12. "Hazardous Waste Destruction," E. T. Oppelt, Environmental Science and Technology, Vol. 20, No. 4, 1986.

13. "Incineration of Hazardous Waste in Power Boilers: Emissions Study Rationale and Test Site Matrix," R. A. Olexsey, Proceedings, Tenth Annual Research Symposium - Incineration and Treatment of Hazardous Waste, U.S. EPA Report No. 600/9-84-022, September 1984.

14. Draft Regulatory Analysis for Proposed RCRA Regulations on Burning of Hazardous Wastes, U.S. EPA, January 1984.

15. Control of Toxic Metal Emissions For Boilers Which Burn Hazardous Waste, U.S. EPA, Office of Solid Waste, 1985.

16. Practical Limitations of Waste Characteristics for Effective Incineration, Draft Report, Peer Consultants, U.S. EPA, Cincinnati, Ohio, September 1985.

17. "Incineration and Cement Kiln Capacity for Hazardous Waste Treatment," Vogel, et al., Proceedings of the 12th Annual Research Symposium: Incineration and Treatment of Hazardous Wastes, Cincinnati, Ohio, April 1986.

18. "Analysis of PIC and Total Mass Emissions from Incineration," Andrew Trenholm, 12th Annual Research Symposium on Incineration and Treatment of Hazardous Waste, Cincinnati, Ohio, April 1986.

19. "Incineration of Liquid Hazardous Waste," U.S. EPA Science Advisory Board, Environmental Effects, Transport and Fate Committee, 1985.

20. A Profile of Existing Hazardous Waste Incineration Facilities and Manufacturers in the United States, U.S. EPA, February 1984 (Available from National Technical Information Service [NTIS], Springfield, VA, 22161, Order No. PB-84-157072).

21. Assessment of Incineration as a Treatment Method for Liquid Organic Hazardous Wastes - Background Report III: Assessment of the Commercial Hazardous Waste Incineration Market, U.S. EPA, March 1985, U.S. Government Printing Office, 1985-526-778/30376.

22. "Hazardous Waste Destruction," E. Timothy Oppelt, *Environmental Science and Technology*, Vol. 20, No. 4, 1986.

23. Assessment of Incineration as a Treatment Method for Liquid Organic Hazardous Wastes - Background Report V; Public Concerns Regarding Land-Based and Ocean-Based Incineration, U.S. EPA, March 1985, U.S. GPO, 1985-526-778/30376.

HAZARDOUS WASTE LANDFILL RESEARCH

U.S.E.P.A. PROGRAM

Norbert B. Schomaker

U.S. Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
Land Pollution Control Division
Cincinnati, Ohio 45268

November 1986

INTRODUCTION

The Land Pollution Control Division (LPCD), Hazardous Waste Environmental Research Laboratory (HWERL), U.S. Environmental Protection Agency (USEPA), in Cincinnati, Ohio, has responsibility for research in solid and hazardous waste management with respect to land disposal of wastes. To fulfill this responsibility, the LPCD is developing concepts and technology for new and improved control systems for solid and hazardous waste land disposal; is documenting the environmental effects of various waste disposal practices; and is collecting data necessary to support implementation of disposal guidelines mandated by The Hazardous and Solid Waste Amendments of 1984 (HSWA). This paper will present an overview of the land disposal research associated with the LPCD hazardous waste program plan.

The performance of treatment, storage, and disposal facilities are being improved to contain the complex wastes being generated by a changing society. These improvements are brought about by the development of control technologies which are useful to the USEPA program offices, Office of Solid Waste (OSW) and Regions, state and local agencies, design engineers and waste management facility operators. The results of these improved control technologies will be the ability to optimize designs, minimize maintenance and overall costs while maintaining a high degree of confidence that the waste management facility will operate as designed. The control technologies being developed or improved take into account region uniqueness, complex waste streams including quality, quantity, and physical state, and a variety of potential designs which will minimize/prevent releases to the environment from waste disposal facilities. These technologies are being laboratory-studied and field-verified to provide the user community with economical, long-lasting systems that will contain the changing waste streams that are being disposed of by traditional, innovative, and high technology industries.

This paper will present an overview of the land disposal research associated with the LPCD hazardous waste program plan and will report the current status of work in the following categorical areas:

HAZARDOUS WASTE FACILITIES - LANDFILLS AND SURFACE IMPOUNDMENTS

1. Cover Systems
2. Waste Leaching/Modification
3. Flexible Membrane Liners
4. Clay Soil Liners
5. Quality Assurance/Quality Construction
6. Expert Systems
7. Corrective Action

NON-HAZARDOUS WASTE FACILITIES

1. Subtitle "D" Facilities

TECHNOLOGY TRANSFER

1. Technical Research Documents

HAZARDOUS WASTE FACILITIES - LANDFILLS AND SURFACE IMPOUNDMENTS

COVER SYSTEMS

The objective of this activity is to develop and evaluate the effectiveness of various cover systems in relation to their functional requirements for actual field application. The primary functional requirements are to minimize moisture infiltration and to promote gas venting. Validation efforts are being performed in the laboratory and field with model work development being pursued for eventual incorporation into a Technical Resource Document (TRD).

The inital laboratory efforts on the study of landfill cover performance have been completed. These recently completed efforts focused on multi-layered cover systems utilizing materials such as a variety of soils, flexible membrane liners and sand drainage blankets. Additional studies may become necessary depending on the results obtained from current field and modeling investigations.

The field efforts being investigated are concerned with the monitoring and modeling of the hydrologic integrity of three multi-layered landfill covers under stable and subsidence conditions. This study monitors infiltration conditions within the constructed cover soil layers and then applied soil moisture, precipitation, and runoff data to verify hydrologic models such as "The Hydrologic Evaluation of Landfill Performance" (HELP) and "The Chemicals, Runoff, Erosion and Agricultural Management System" (CREAMS).

The TRD is a compilation and presentation of best available technology and information on methods to control infiltration, to improve long-term cover performance and on the development of construction, maintenance, and inspection criteria to improve clay and flexible membrane cover performance, cover drainage and maintenance free vegetative cover systems. The initial TRD entitled, "Design, Construction, and Maintenance Cover Systems for Hazardous Waste" was published in 1984. This document can be ordered from the National Technical Information Service (NTIS). The NTIS stock number is PB81-166-340. This TRD is currently being updated and should be available for publication in the spring of 1987. A technical handbook entitled, "Covers for Uncontrolled Hazardous Waste Sites" EPA/540/2-85/002 dated September 1985 has been published under the Superfund program. This technical handbook provides guidance for regulatory personnel involved with Superfund sites but could be also used at other controlled sites.

WASTE LEACHING/MODIFICATION

The objective of this activity is twofold: (1) to develop and evaluate laboratory techniques for working with a sample of a waste or a mixture of waste to predict the composition of actual leachates obtained under field conditions and (2) to evaluate the effectiveness of solidification/stabilization and encapsulation processes for improved handling, surface area reduction, limiting solubility, detoxifying pollutants and predicting performance with time. Results from laboratory and model predictions are being compared with results from pilot-scale and field-scale work to develop better evaluation procedures and an up-dated TRD on waste leaching and waste modification.

The laboratory efforts currently being pursued relating to waste modification include the study of solidification/stabilization mechanisms, whether due to physical entrapment or chemical interaction. This effort is determining in what phase(s) of the binder-waste matrix the contaminants are held. Microscopy and leaching procedures are used with organic and inorganic wastes. In addition, various solidification/stabilization processes are being assessed and evaluated to determine the effects of interfering materials (organics and inorganics) on process and product performance. Evaluation of the waste modification techniques includes leaching to determine concentrations of contaminants released and physical measurements (e.g., freeze-thaw, wet-dry) to assess durability of the solidified waste.

Currently no field efforts are being pursued in this research area. Future studies may become necessary depending on the results obtained from current investigations.

The original TRD on "Solid Waste Leaching Procedure" (SW-924) has been updated and a 2nd edition entitled, "A Procedure for Estimating Monofilled Solid Waste Leachate Composition" (SW-924) is being reviewed by OSW. Final publication is expected by March 1987. In addition to the leaching procedure TRD, a TRD entitled, "Landfill and Surface Impoundment Performance Evaluation" (SW-869) relating to leachate generation was published in 1984 and can be obtained from the NTIS. PB81-166-357 is the NTIS stock number. The original TRD on "Guide to the Disposal of Chemically Stabilized and Solidifed Wastes" (SW-872) was published in 1984 and can be ordered from NTIS. The NTIS stock number is PB81-166-505.

This original stabilization TRD has been updated as a technical handbook for Superfund sites. This document entitled, "Handbook for Stabilization/Solidification of Hazardous Wastes," EPA/540/2-86/001 dated June 1986 has been published.

FLEXIBLE MEMBRANE LINERS

The objectives of this activity are to evaluate the effectiveness of synthetic membranes or flexible membrane liners (FML's) as liners and surface caps to contain or minimize leachate movement and prevent moisture infiltration, and to develop means to predict the long-term performance of liners.

The laboratory efforts include the evaluation of upward hydrostatic forces on FML's and loading points and also for the development of field verification data for flexible membrane liners (FML's). The research of upward hydrostatic forces is evaluating the puncturability effects of fixed point loads in a subgrade under slowly increasing water pressure. Room and elevated temperatures are being used to accelerate the potential reaction. The benefits of using geotextiles to prevent the puncture are also being evaluated.

The effort to develop field vertification data for FML's has met with limited success. Results indicate laboratory tests, such as Method 9090, can predict the chemical compatibility of FMLs. However, additional field data are required to assess long-term performance and environmental stress cracking.

A major revision of the TRD (SW-870) "Lining of Waste Impoundments and Disposal Facilitlies" is underway. New information is now available on improved techniques for estimating chemical compatibility, seam quality, and understanding field failure mechanisms. The very rapid increase in use of geotextiles and geonets in lining systems necessitates a major revision to the TRD to include these topics. The draft revision is scheduled for the fall of 1987 with final publication in early 1988.

CLAY SOIL LINERS

The objective of this activity is to evaluate the effectiveness of compacted clay soils used in surface covers and bottom liners for minimizing infiltration of water and escape of leachate. Results of these laboratory and field evaluations are then used to develop procedures for evaluating designs and predicting long-term performance so that liners can be constructed to perform in accordance with design specifications.

Laboratory efforts are evaluating the effects of organic chemicals and inorganic leachates on the structure and permeability (hydraulic conductivity) of compacted clay soils and comparing the results with data collected from field sites. Generally, concentrated solutions of organic and inorganic chemicals increase the permeability of clay soils and cause them to be unsuitable for controlling liquid movement in landfills. Dilute aqueous solutions of chemicals and some field leachates do not affect the permeability of clay soils, at least in short-term tests. The critical concentration at which a chemical will begin to affect soil permeability is not known for all chemicals and leachates.

Laboratory efforts are also examining: (a), the measurement and significance of effective porosity to determine if this soil property can be used in regulating soil liners; (b), the precision and bias of field and laboratory permeability (hydraulic conductivity) measurements; (c), measurement of adsorption coefficients in batch soil studies for use in designing liners to retard the movement of pollutants.

Field studies using clay soil liner test sections constructed with actual equipment and soil handling procedures are examining: (a), the ability of laboratory measurements to predict actual field permeability; (b), usefulness of procedures for predicting liquid transit time, i.e., the time for liquids such as water, leachate, etc., to move through the liner; (c), methods for optimizing construction unit operations to achieve permeability of 10^{-7} cm/sec.

Technical Resource Documents have been developed to collect and analyze information on design, construction, and evaluation of clay liners and information on use of batch adsorption procedures to design clay liners for pollutant removal. These TRD's have been published for public comment; revised versions will be published.

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

QA/QC has become an area of increased importance and emphasis in the design and construction of land disposal facilities. It is a critical element in the fabrication of materials, e.g., FML, drainage nets, etc., design and construction of system components, e.g., covers, clay and FML liners, drain systems, etc., and the construction of the whole facility. The design, implementation and adherence to a strong QA/QC plan are among the major factors in assuring that land disposal facilities successfully perform as they are designed to do.

This program area has been addressed indirectly in several previous projects dealing with soil liner hydraulic conductivity measurements, FML seaming and inspection requirements, subsurface preparation, liner bedding requirements, and similar activities. The first project to address this area directly was the preparation of a technical guidance document entitled, "Construction Quality Assurance for Hazardous Waste Land Disposal Facilities," EPA530/SW/85/021, which presents summaries of state-of-the-art technologies and evaluation technologies determined to constitute good engineering designs, practices, and procedures. Upon publication in late 1986, it will support the Resource Conservation and Recovery Act (RCRA) TRD's and Permit Guidance Manuals by describing current technologies and methods for designing hazardous waste facilities and for evaluating the performance of the facility design. The document discusses QA/QC requirements in foundations, dikes, low permeability soil liners, flexible membrane liners, leachate collection systems, and final cover systems.

Because QA/QC is a complex area, the research continuing in FY'87 will proceed at a deliberate and reasonable pace. HWERL will keep abreast of QA/QC activities being performed by other research organizations so as additional information becomes available on sampling requirements and factors critical in fabrication and construction of facilities it can be added to the guidance.

EXPERT SYSTEMS

The objective of this activity is to develop user friendly computer based systems that will assist the permit writer in evaluating a permit for treatment, storage and disposal facilities. These systems will emulate the decision processes of subject specialists (experts) by incorporation of their heuristic rules they use to arrive at a particular decision in their specialized area.

The research to date includes a fundamental study to determine the sequence of developing the system. Priorities for individual permit components, e.g., FML chemical compatibility, closure, waste analysis, etc. were identified.

Research is underway on FML chemical compatibility, surface impoundment evaluation, subsidence, and waste analysis. These modules should be available for testing in early 1987. The module on facility-closure and post-closure plans system have been initiated as well as construction quality assurance. These later two modules should be available for testing in 1988.

The TRD developed in this area, EPA/530-SW-84-009/10 "The Hydrologic Evaluation of Landfill Performance (HELP) Model," is being updated to incorporate the two-dimensional aspects of landfill cover systems and recently acquired field data. The field data is being used to calibrate and refine the model. Final publication of these documents is expected in late 1987.

CORRECTIVE ACTION

Corrective action is required to clean up releases from land disposal sites that have adversely affected groundwater. The applicable technologies would be similar to those in use at Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites where subsurface water has been contaminated. Although described as repairs or maintenance, corrective actions are also required in other parts of the regulations. Emergency repairs of covers, liners, and leachate systems during the active life of a disposal site are required by all treatment, storage, and disposal facilities.

Corrective action will involve identifying problems at waste disposal units that cause releases to the environments and applying engineering and management methods to correct the problems. HWERL will closely follow OSW efforts to set up procedures for determining releases of pollutants form RCRA facilities, to develop guidance in setting up assessments, and to initiate needed assessments.

NON-HAZARDOUS WASTE FACILITIES

SUBTITLE "D" FACILITIES

The objectives of this activity are to characterize wastes, leachates, and air emissions from municipal solid waste (non-hazardous) processing and disposal facilities and from large-volume waste disposal facilities, and assess control methods. This research is being conducted to support legislative requirements of HSWA that the Agency review and modify, if necessary, the current criteria being used to manage non-hazardous municipal, commercial, and mining wastes (Subtitle "D").

Laboratory studies include the exploration of chemical and biological methods for rapid stabilization of municipal solid waste sites in an attempt to render them and their leachates inactive or less harmful to the environment. Recirculation, soil filters, and other methods of treatment are being investigated in conjunction with stabilization methods. Experimentation with the control of methane from municipal solid waste by lime injection is being conducted to measure the gas production rates and quantities, measure leachate volumes and composition, and compare the lime treated gas generation to previous results from untreated simulators.

Modeling efforts include the development of an improved model for predicting leachate quantity and quality and the use of previously developed models which predict gas migration to design gas controls and develop general gas control design guidance.

Current field studies are identifying the types of problems that occur at Subtitle "D" facilities, review current practices for dealing with problems, and suggest potential technologies for correcting problems. Detailed chemical analyses of liquid phases of municipal landfill gas condensate are being performed to determine if these different liquid phases have any hazardous waste characteristics. Samples are also being taken of ash residuals from actual municipal waste combustion facilities. These residuals are being analyzed to determine their levels of hazardous constituents.

TECHNOLOGY TRANSFER

TECHNICAL RESEARCH DOCUMENTS

Technology transfer encompasses the collection, documentation, and dissemination of scientific and technical information, including (a), data on the performance and costs of using the technology, (b), the transformation of research and technology into processes, products, and services that can be applied to public or private needs and (c), the secondary application of research or technology developed for a particular mission that fills a need in another environment.

The technology transfer requirement is being met with the publication of the TRD's and Handbooks, the presentation of technical seminars, and by direct technical assistance.

Assessment of a Prototype System
For Pyrolysis of Refused Derived Fuel

by

Stephen Thorndyke
Ontario Research Foundation

for presentation at

Ontario Ministry of the Environment
Technology Transfer Conference

Sheraton Centre, Toronto
December 8 & 9, 1986

ASSESSMENT OF A PROTOTYPE SYSTEM FOR PYROLYSIS OF REFUSE DERIVED FUEL

EFW Systems Incorporated have developed and constructed a prototype unit to pyrolyse refuse derived fuel (RDF), with the intent of using the pryrolysis gases as an engine fuel to generate electricity and as a source of process heat for the pyrolyser. An assessment of the prototype unit has been made to characterize the process and compare emissions with conventional municipal solid waste (MSW) incineration techniques.

The sampling and analytical program is briefly discussed, covering sampling and analytical methodologies, process operating results, composition of the pyrolysis gas fuel and emissions in the pyrolysis gases. Data are presented to show the impact on air quality if pyrolysis gases were emitted directly to the atmosphere. An approximate energy balance for the unit shows that process modifications would be required to produce significant amounts of pyrolysis gas for use as an engine fuel.

INTRODUCTION

With increased difficulties in locating suitable landfill sites for municipal refuse disposal, alternative disposal methods are being pursued as an essential component of most waste management programs. These methods generally can be classified as either biological or thermochemical conversion. The thermochemical conversion methods are often accompanied by energy recovery and offer the advantage of greatly reducing the volume of the refuse. For example, complete combustion is often used to generate steam for industrial use, whereas partial combustion is used to produce fuels or chemical feedstock. Complete combustion facilities were initially developed many years ago and are currently in widespread use. There are some full-scale partial combustion facilities in operation but most of these processes are still in the developmental stage.

Air pollution is recognized as the potentially most serious limitation to the use of complete combustion facilities to dispose of municipal refuse. Numerous studies have identified particulate matter, acid gases, trace organics and trace metals as contaminants which may be emitted in significant amounts. However, with appropriate combustion conditions and air pollution control devices, studies have shown that emission rates of these contaminants can generally be maintained within current Ontario air emission standards and guidelines. Few studies have been carried out to investigate potential air pollution problems associated with partial combustion processes. One of these partial combustion processes is pyrolysis, and a study, sponsored by the Ontario Ministries of Energy and the Environment, was carried out to assess the performance and determine the emissions of airborne contaminants for a pyrolysis system.(1) Pyrolysis has the advantage that a fuel is produced which can be stored and transported. There may also be cost advantages over conventional municipal refuse incinerators.

PYROLYSIS PROCESS

The refuse pyrolysis process involves heating the refuse in the absence of air to a temperature of about 800°C or higher.(2). The gaseous product, containing hydrogen, carbon dioxide, carbon monoxide, methane and water vapour as the major components in varying amounts, has a heating value of about 20 MJ/kg on a dry basis. This gas, usually termed a medium energy gas, requires treatment to remove impurities such as particulate matter, gaseous impurities and condensible organics before it can be used as a fuel or for other purposes.

The pyrolysis system investigated in this study is a prototype unit, built by EFW Systems Incorporated. This is a continuous moving-bed system with a nominal feed rate of 1000 kg/h, although the feed rate during the study was about 545 kg/h of shredded refuse with inorganic components removed, or refuse derived fuel (RDF), and containing about 10% moisture.

In this prototype unit, indirect propane combustion is used to initiate pyrolysis of the RDF and the pyrolysis gases are flared to the atmosphere without further treatment, as shown in Figure 1. During commercial operation, a portion of the pyrolyser gases would be directly combusted to provide heat for pyrolysis initiation and the remainder would be combusted in a spark-ignited Waukesha gas engine to generate about 350 kW of electricity.

STUDY OBJECTIVES

The overall objective in constructing and evaluating the EFW pyrolyser was to determine if this particular pyrolysis process is a viable alternative to conventional incineration for disposing of RDF.

Specific objectives of the test program carried out by ORF were as follows:

- to characterize the major gaseous components in the EFW pyrolysis gases so that the suitability of using this product as an engine fuel, after the removal of impurities, can be assessed.
- to measure the concentrations and emission rates of potential contaminants in the pyrolysis gases as a basis for an environmental assessment of the EFW pyrolysis process.
- to determine the conversion efficiency and energy efficiency of the EFW pyrolyser.

TESTING PROGRAM

On the basis of results from previous emission tests at refuse combustion facilities,(3) the following groups of potential contaminants in the pyrolysis gases were included in the present study.

- particulate matter
- acid gases
- dioxins and furans
- PCB's, chlorobenzenes and chlorophenols
- polycyclic aromatic hydrocarbons
- trace metals

Of principal concern to the study were dioxins (polychlorinated dibenzo-p-dioxins) and furans (polychlorinated dibenzofurans). Dioxins and furans in the flue gases at conventional refuse incinerator originate either from their presence in the refuse, (4) or they are formed during conventional refuse combustion from precursor compounds such as PCBs, chlorobenzenes and chlorophenols. Studies have shown that amounts of these compounds in incinerator emissions can be significant compared with the Ontario provisional guidelines, but with good combustion conditions (that is: high temperatures, good mixing and adequate residence time), emission rates can be greatly reduced. Polycyclic aromatic hydrocarbons, some of which are considered to be carcinogenic, are also generally present in the flue gases from refuse incineration. All of these trace organic compounds were considered in the emission study.

Particulate matter, acid gases, and trace metals are often emitted in significant amounts from refuse combustion, but, with appropriate air pollution control equipment, concentrations can be reduced to levels below Ontario environmental standards and guidelines. In addition to sampling the pyrolysis gases, samples of the pyrolyser ash were collected for analysis.

SAMPLING AND ANALYTICAL

Except for the gaseous components of the pyrolyser gases, pyrolysis gas sampling was carried out using modified MOE Method 5 sampling trains.(5) A conventional Method 5 train is shown in Figure 2.

A single train was used for all the trace organic compounds. In a preliminary test, an ASME(6) version of the train was used in which the flue gas sample was passed successively through a probe, particulate filter, Amberlite XAD-2 resin cartridge and impinger solutions.

This train is generally accepted as the standard method for trace chlorinated organic sampling. This test was unsuccessful, however, because organic compounds quickly condensed in the resin cartridge and restricted the sample flow. Therefore, a different train was used in succeeding tests, which consisted of a probe, particulate filter, impinger solution and Florisil adsorbent cartridge. This train was developed by the Ontario Ministry of the Environment a few years ago and has been shown to be effective for sampling trace chlorinated organics.(4)

Particulate matter, acid gases and trace metals were sampled in a single train. The flue gas sample was passed successively through a probe, particulate filter, dilute sodium hydroxide impinger to collect acid gases and some metals (antimony, arsenic, selenium and tellurium), dilute nitric acid impingers to collect most metals, and an acidified potassium permanganate solution to collect mercury.

Gaseous concentrations were determined using either gas chromatography or continuous analyser techniques. Hydrogen, carbon monoxide, carbon dioxide, methane, nitrogen and C-2 hydrocarbons were analysed by gas chromatography using a Carbosieve SII column and a thermal conductivity detector. Hydrogen sulfide was analysed by gas chromatography, combined with a flame photometric detector. Tedlar bags (polyvinyl fluoride) were used to collect samples for this analysis. Continuous analysers were used for oxygen, sulfur dioxide and nitrogen oxides analyses.

All trace organic analyses of the flue gas samples were carried out using gas chromatography/mass spectrometry techniques and procedures described in the ASME draft method for chlorinated organics sampling.

Most of the trace metal analyses were done by d.c. plasma atomic emission spectroscopy. Solutions were analysed directly, whereas particulate samples were digested with nitric acid and aqua regia before analysis. Silver was analysed by flame atomic absorption spectrophotometry and mercury by cold vapour atomic absorption spectrophotometry. Arsenic, antimony, selenium and tellurium were analysed by hydride generation atomic absorption.

Acid gases were analysed by ion chromatography. Cyanide was determined by a colorimetric method and ammonia was determined by reaction with Nesslar reagent.

Ultimate analyses were carried out on both the pyrolyser ash and the pyrolyser gas particulate matter.

Three separate tests were completed and average results from these tests were used to assess the pyrolyser performance.

RESULTS

Average major gaseous component concentrations in the pyrolyser gases are presented in Table 1. Hydrogen predominates with lesser amounts of methane, carbon monoxide and carbon dioxide. Other identified components are present in minor amounts. Unidentified components are believed to include residual moisture, hydrocarbons and acid gases.

In Table 2, the concentrations of the contaminants identified in the flue gases are identified. To determine the relative importance of these contaminants, the concentrations are compared with the Ontario Regulation 308 maximum permitted point-of-impingement concentrations(7) (8) as ratios of the flue gas concentration to the impingement concentration. These ratios essentially indicate how much the flue gases must be diluted to bring the impingement concentrations within the regulations, but are used in this study to indicate which contaminants are of most concern.

The highest ratio is for particulate material. However, it is anticipated that almost all of the particulate material would be removed in a scrubbing device before using the gases as a fuel. Of the gases and acid gases, hydrogen sulfide and carbon monoxide have the highest ratios. The carbon monoxide would be converted to carbon dioxide and the hydrogen sulfide to sulfur dioxide during utilization of the pyrolysis gases.

The highest metal ratio is for lead. Although no detectable amounts of beryllium were observed in any of the samples, the relatively high detection limit and very stringent emission regulation results in a high concentration ratio. From the proportions of the metals retained on the particulate filter during sampling, it is apparent that almost all the metals could be removed by scrubbing. An exception may be mercury because 98% appeared to be present as a vapour, consistent with its known high volatility.

In Table 3, emission factors for the pryolyser are compared with emission factors for MSW incineration from a recent study at a modern, efficient two-stage modular incinerator. As expected, the particulate emission factor is much higher for pyrolysis. Lower emission factors during pyrolysis occurred for hydrogen chloride and, in particular, dioxins and furans. For dioxins and furans, the lack of oxygen in the pyrolyser may be responsible for the low emission factors. Because of the very low levels present, emission factors for the dioxins and furans are essentially based upon the detection limits of the sampling and analytical methods. A very much higher emission factor was obtained for PAHs with pyrolysis.

Ultimate analyses for the fly ash and pyrolyser ash, Table 4, show high carbon analyses indicating conversion of carbon to carbon monoxide and carbon dioxide during pyrolysis was not very efficient.

Table 5 represents a material balance for the major elemental components of the refuse derived fuel, carbon, hydrogen and oxygen, during pyrolysis. Input values are based on typical values for refuse derived fuel,(9) combined with experimentally determined moisture contents. The data indicate 29% of the carbon and 51% of the hydrogen in the dry feed are converted into dry pyrolysis gases.

Table 6 summarises the composition of the dry pyrolyser product gas after treatment to remove all impurities. The higher heating value is 15.0 MJ/Nm^3 (400 Btu/scf) or 21.3 MJ/kg (9,200 Btu/lb). The dry pyrolysis gases represent about 28% of the original RDF feed material and the total pyrolysis gases, including water vapour, represent about 53% of the original RDF feed material.

An approximate energy balance, Table 7, indicates energy recovery in the pyrolysis gases is only 37%. A more favorable energy balance could be obtained by improved burnout of the refuse derived fuel, a reduction in equipment heat losses and recovery of energy during cooling of the grate ash, pyroloysis gases or combustion gases.

DISCUSSION

Results of the ORF study have shown that, under the conditions prevailing during sampling of a prototype unit, the EFW pyrolyser produces raw pyrolysis gases which contain high particulate and gaseous impurity concentrations, 141 g/m^3 and 12.8% by volume on a dry basis, respectively, in addition to a high moisture content of 40.7% by volume.

In commercial use, it is anticipated that a portion of the pyrolysis gases would be combusted to provide process heat for sustaining pyrolysis, and the remainder would be used as an engine fuel to generate electricity. Because of the presence of moisture, particulate and gaseous impurities, treatment of the raw pyrolysis gases will be necessary before use as a fuel. Without treatment, excessive contaminant emissions to the atmosphere and damage to the engine likely would result.

If all the moisture and impurities are removed during the pyrolysis gas treatment, a medium energy fuel of the following composition would result: 41% hydrogen, 21% carbon monoxide, 22% methane and 17% carbon dioxide by volume. Additional treatment may be necessary to increase the higher heating value, or to adjust the octane rating before it can be used as an engine fuel.

A comparison of potential contaminant concentrations in the raw pyrolysis gases with the maximum point-of-impingement concentrations permitted by the standards and guidelines in Regulation 308 of the Ontario Environmental Protection Act indicate that the contaminants of most concern (those with the highest required diluting ratios) were particulate matter, carbon monoxide, hydrogen sulfide, beryllium, lead and sulfuric acid. These contaminants may cause the standards and guidelines to be exceeded if the raw pyrolysis gases were emitted directly to the atmosphere without dilution. Although there are no standards or guidelines for PAH compounds, the substantial amounts of these compounds present may pose a more serious threat to the environment than any of the other potential contaminants.

With adequate flue gas control for particulate matter and acid gases, the potential threat to the environment by the pyrolysis gas contaminants would be greatly reduced. After combustion of the pyrolysis gases, either to provide process heat or as an engine fuel, it appears the regulated contaminants of most concern will be mercury, particulate matter, sulfur dioxide and perhaps beryllium. Concentrations would be low, however, and it appears that only a relatively short stack would be required for adequate dispersion of the combustion gases. Most of the metals and PAH compounds would be removed during particulate control since they are generally associated with particulate material. The amount of PAH remaining in the combustion gases will depend very much on the temperature and residence time during combustion.

Compared with the disposal of MSW in a modern two-stage incinerator, the raw EFW pyrolyser gases exhibit much higher emission factors for PAH compounds, carbon monoxide and particulate matter. An important feature of the pyrolysis gas composition is the virtual absence of trace chlorinated organics, particularly dioxin and furan compounds, together with their known precursors during combustion. Also, amounts of hydrogen chloride may be much lower with pyrolysis.

To summarize, the following conditions would have to be met to avoid adverse environmental effects from the EFW pyrolyser:

- the raw pyrolysis gases are toxic and must not be released directly to either the atmosphere or the work place.
- a high efficiency control system is required to remove most of the particulate and acid gas contaminants from the raw pyrolysis gases before use as a fuel.
- combustion of the cleaned pyrolysis gases must involve sufficiently high temperatures and long residence time to destroy the remaining PAH compounds.

From material balance calculations, the reduction in dry weight of the RDF during pyrolysis will be approximately 56%, and the conversion of carbon into gases, particulate carbon (pyrolysis gas particulate matter) or condensible compounds will be 46%. Theoretically, the weight reduction could be as high as 91% if no organic carbon or hydrogen remain in the ash, and this is the weight reduction which might be expected with conventional MSW incineration. However, maximizing the weight reduction is not necessarily the most important criterion in judging the performance of the pyrolyser, since the cost of any attempts to increase the weight reduction, such as higher process temperatures or increased solids residence time, must be weighted against reduced costs for landfill requirements.

An approximate energy balance indicates that only 25% of the energy in the refuse derived fuel is recovered in the cleaned pyrolysis gases, and this energy would be mostly required to initiate pyrolysis, with little, if any, available for electricity generation.

This situation may be overcome to some extent by improving the conversion of carbon in the grate ash and particulate emission, recovery of sensible heat in the pyrolyser and combustion gases and reducing equipment heat loses.

Thus, it is concluded that the prototype EFW pyrolyser emits significant quantities of some environmental contaminants and has an unfavourable energy balance. However, it may be possible to overcome these problems in a commercial unit, provided that it is economical to install adequate pollution control and energy recovery equipment.

REFERENECES

(1) "Evaluation of a Prototype ROF Pyrolyser", S. Thorndyke, ORF Report No. 46-10439. January 22, 1986.

(2) "Thermal Systems for Conversion of Municipal Solid Waste, Volume 5: Pyrolytic Conversion: A Technology Status Report." J.L. Kuester. U.S. Department of Energy Report No. DE84003664. June 1983.

(3) "The National Incinerator Testing and Evaluation Program: Two-Stage Combusiton (Prince Edward Island)." Environment Canada Report No. EPS/3/UP/1. September 1985.

(4) "Determination of Chlorinated Dibenzo-p-Dioxins, Chlorinated Dibenzofurans, Chlorinate Biphenyls, Chlorobenzenes and Chlorophenols in Air Emissions and Other Process Streams at SWARU in Hamilton." Ministry of the Environment Report No. ARB-02-84-ETRD.

(5) "Source Testing Code". Report No., ARB-TDA-66-80. Ontario Ministry of the Environment. 1980.

(6) "Sampling for the Determination of Chlorinated Organic Compounds in Stack Emissions." American Society of Mechanical Engineers. Draft Method 1984.

(7) "Environmental Protection Act - Regulation 308". Revised Regulations of Ontario, 1980. December 1982.

(8) "List of Tentative Standards, Guidelines and Provisional Guidelines for Air Contaminants." Ontario Ministry of the Environment, Air Resources Branch. July 1984.

(9) "Thermal Systems for Conversion of Municipal Solid Waste, Volume 4: Burning Refuse-Devrived Fuel in Boilers: A Technology Status Report." F. Hasselriis. U.S. Department of Energy Report No. DE84010490. March 1983.

FIGURE 1

Simplified Diagram of the EFW Pyrolyser

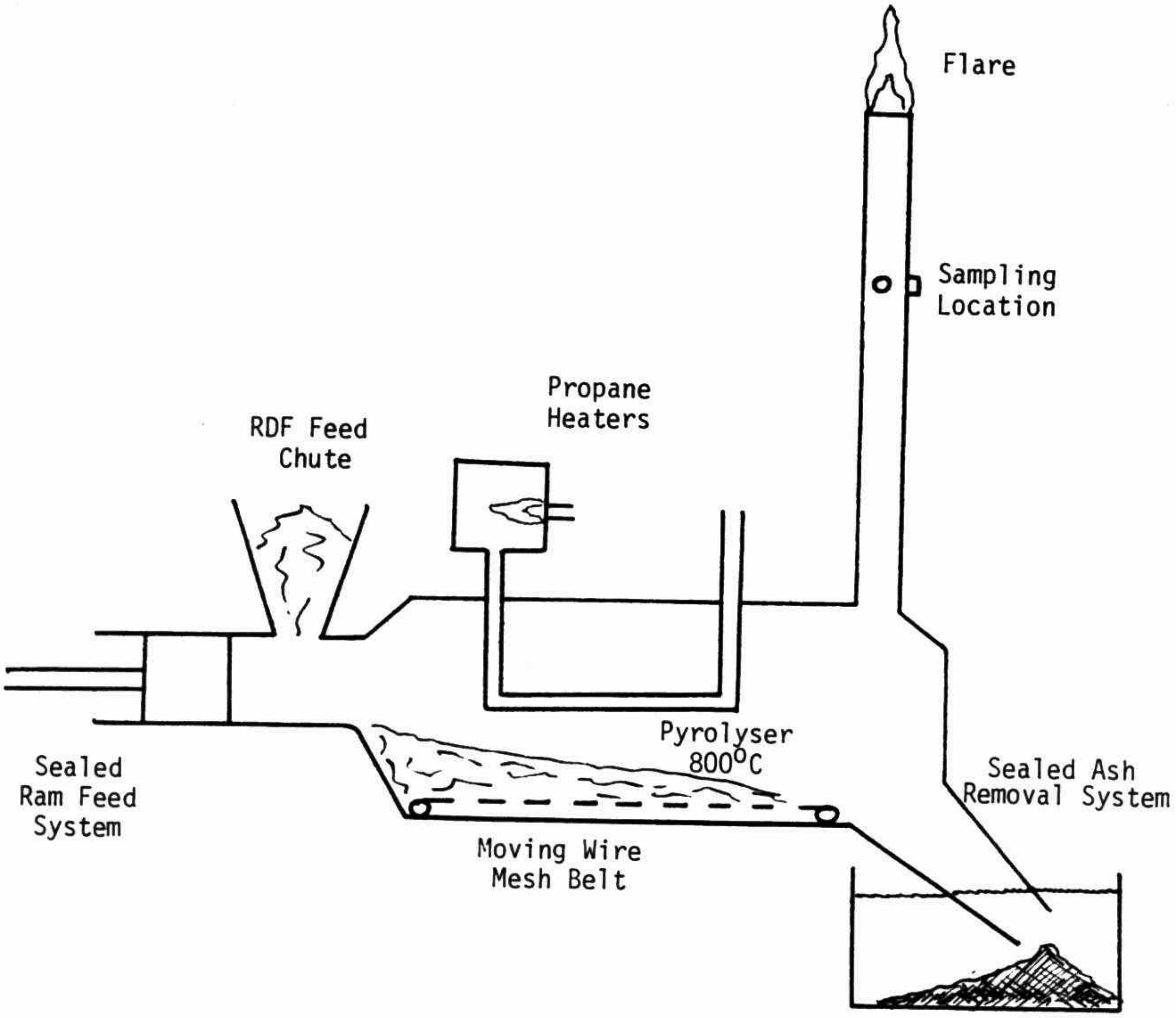


FIGURE 2

Refuse Pyrolysis Emissions

Method 5 Sampling Train

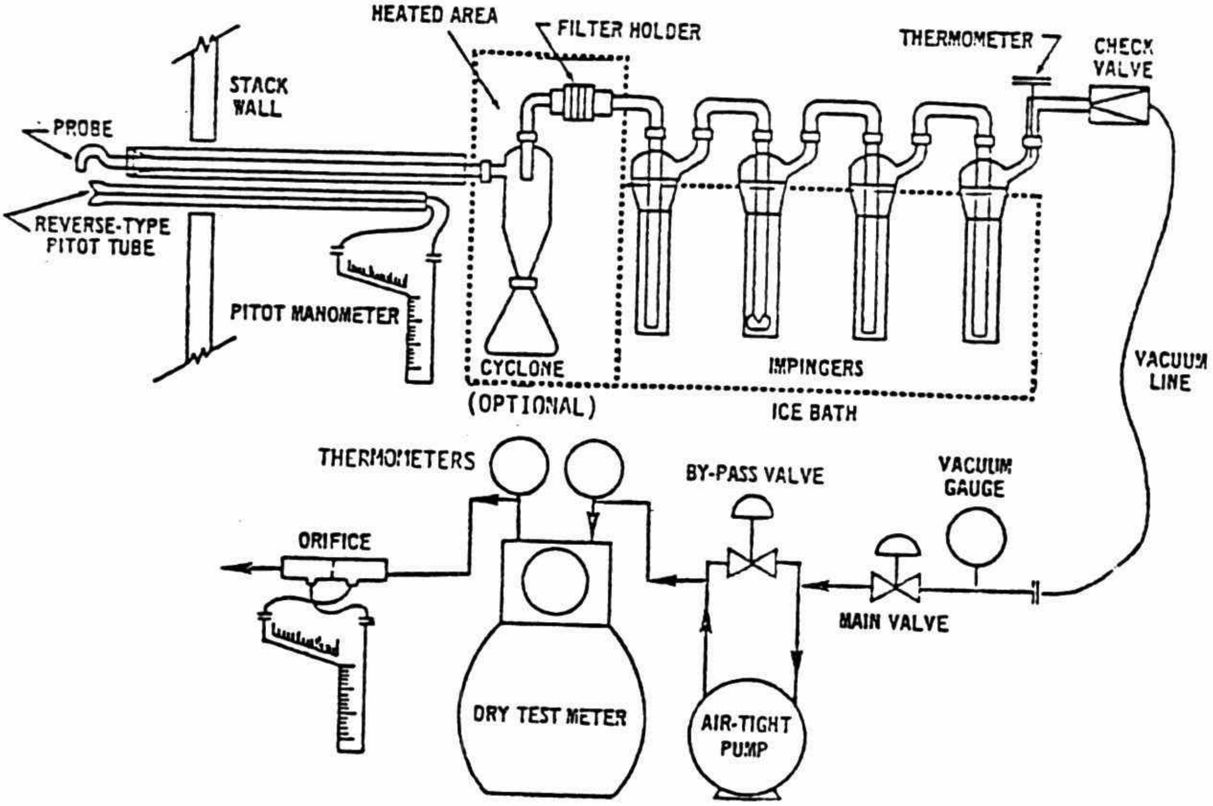


TABLE 1

Refuse Pyrolysis Emissions

Average Dry Gaseous Component Concentrations

Gas		Average Concentration %
Hydrogen		35.56
Methane		19.09
Carbon Monoxide		17.85
Carbon Dioxide		14.66
C2 - Hydrocarbons		1.42
Nitrogen		0.88
Ammonia		0.35
Oxygen		0.19
Hydrogen Sulfide		0.11
Hydrogen Cyanide		0.10
Sulphur Dioxide		0.03
Other*		9.76
	Total:	100.0

*Including Residual Moisture, Hydrocarbons and Acid Gases.

TABLE 2

Refuse Pyrolysis Emissions

Comparison of Flue Gas Emissions with Environmental Protection Act Regulation 308 Standards

Contaminant	Flue Gas Concentration	Maximum Impingement Concentration	Concentration Ratio
Particulate	141 g/Nm^3	100 µg/m^3	1410000
NH_3	2.5 g/Nm^3	3600 µg/m^3	686
CO	205 g/Nm^3	6000 µg/m^3	34083
HCN	1.1 g/Nm^3	1150 µg/m^3	946
H_2S	1.5 g/Nm^3	30 µg/m^3	50000
NO_2	0.02 g/Nm^3	500 µg/m^3	40
SO_2	0.65 g/Nm^3	830 µg/m^3	783
HCL	8.2 mg/Nm^3	100 µg/m^3	82
HF	0.54 mg/Nm^3	4.3 µg/m^3	126
HNO_3	4.1 mg/Nm^3	100 µg/m^3	41
H_3PO_4	2.7 mg/Nm^3	100 µg/m^3	27
H_2SO_4	202 mg/Nm^3	100 µg/m^3	2017
Sb	7.4 mg/Nm^3	75 µg/m^3	99
As	0.6 mg/Nm^3	15 µg/m^3	40
Be	0.2 mg/Nm^3	0.03 µg/m^3	6667
B	30 mg/Nm^3	100 µg/m^3	300
Cd	2.4 mg/Nm^3	5 µg/m^3	480
Cr	1.4 mg/Nm^3	5 µg/m^3	280
Cu	5.5 mg/Nm^3	100 µg/m^3	55
Pb	26 mg/Nm^3	10 µg/m^3	2600
Mn	20 mg/Nm^3	100 µg/m^3	200
Hg	2.1 mg/Nm^3	5 µg/m^3	420
Ni	2.9 mg/Nm^3	5 µg/m^3	580
Se	0.1 mg/Nm^3	20 µg/m^3	5
Ag	0.2 mg/Nm^3	3 µg/m^3	67
Te	0.1 mg/Nm^3	30 µg/m^3	3
Sn	2.2 mg/Nm^3	30 µg/m^3	73
V	0.9 mg/Nm^3	5 µg/m^3	180
Zn	23 mg/Nm^3	100 µg/m^3	230
PCDD + PCDF	19 ng/Nm^3	450 pg/m^3	42
PCBs	13 µg/Nm^3	450 ng/m^3	29

TABLE 3

Refuse Pyrolysis Emissions

Comparison of Refuse Pyrolysis and Combustion Emissions

Contaminant	Emission Factor Units	RDF Pryolysis Emission Factors*	MSW Incineration Emission Factors*
Particulate	g/kg	75.4	1.3
Hydrogen Chloride	mg/kg	4.3	6770
Antimony	mg/kg	3.9	3.5
Cadmium	mg/kg	1.3	5.9
Chromium	mg/kg	0.8	0.3
Lead	mg/kg	13.7	84.0
Mercury	mg/kg	1.1	4.3
Nickel	mg/kg	1.5	1.5
Dioxins	ng/kg	9.5	658
Furans	ng/kg	6.5	877
PCBs	µg/kg	6.7	5.3
PAHs	mg/kg	1100	0.05

*Dry Basis

TABLE 4

Refuse Pyrolysis Emissions
Ultimate Analysis of the Pyrolyser Ash

	Dry Analysis, % By Weight	
	Fly Ash	Pyrolyser Ash
Carbon	92.5	44.1
Hydrogen	2.0	1.5
Ash*	5.5	43.9
Nitrogen	-	1.1
Chlorine	-	0.4
Sulfur	-	0.5
Oxygen	-	8.5

* By Difference

TABLE 5

Refuse Pyrolysis Emissions

Elemental Material Balance

	Carbon g/s	Hydrogen g/s	Oxygen g/s
Input			
Refuse	61.74	8.22	50.95
Moisture		1.64	13.09
Output			
Hydrogen		2.04	
Carbon Monoxide	6.14		8.18
Methane	6.56	2.19	
Carbon Dioxide	5.04		13.44
Oxygen			0.17
Moisture		3.77	30.13
Flue Gas Particulate	9.55	0.19	
Grate Ash*	34.45	1.35	12.12
Total Input/Output	61.74	9.86	64.04

* By Difference

TABLE 6

Refuse Pyrolysis Emissions

Properties of the Dry Gaseous Product

Component	Composition	
Hydrogen	40.8% vol.	4.8% wt.
Carbon Monoxide	20.5% vol.	32.8% wt.
Methane	21.9% vol.	20.3% wt.
Carbon Dioxide	16.8% vol.	42.1% wt.
Total:	100.0% vol.	100.0% wt.
	Emission Rate	Emission Factors
Hydrogen	2.0 g/s	0.013 g/g
Carbon Monoxide	14.0 g/s	0.092 g/g
Methane	8.5 g/s	0.056 g/g
Carbon Dioxide	18.0 g/s	0.119 g/g
Total:	42.5 g/s	0.281 g/g
Higher Heating Value	15.03 MJ/Nm^3 (400 Btu/scf)	21.33 MJ/kg (9,200 Btu/lb)

TABLE 7

Refuse Pyrolysis Emissions
Approximate Energy Balance

Energy Input

RDF Heat Content = 2.48 MW
Propane Heat Content = 1.13 MW

Total = 3.61 MW

Energy Output

Pyrolysis Gas Heat Content = 0.91 MW

Pyrolysis Gas Sensible Heat = 0.25 MW

Grate Ash Heat Content = 0.34 MW

Fly Ash Heat Content = 0.35 MW

Propane Combustion Gas Sensible Heat = 0.61 MW

Miscellaneous* = 1.15 MW

Total = 3.61 MW

* Including grate ash sensible heat, equipment heat losses and heat content of unidentified pyrolysis gas components.

MUNICIPAL SOLID WASTE FEASIBILITY OF GASIFICATION WITH PLASMA ARC

G.W. Carter
Resorption Canada Ltd.,
Ottawa, Ontario

MUNICIPAL SOLID WASTE
FEASIBILITY OF GASIFICATION WITH PLASMA ARC

Presented to
1986 Technology Transfer Conference
December 8, 1986

BACKGROUND

Resorption Canada Limited (RCL) is a private high tech firm which was federally incorporated to design, fabricate, market and service industrial systems utilizing plasma arc technology. The Company is heavily R&D oriented since this technology is still relatively new to the Canadian industrial marketplace. Plasma arc has potential wide applicability in business and industry where a controlled source of intense heat is required.

RCL operates a plasma research facility in Ottawa, Ontario in which it conducts tests, research experiments and demonstrations utilizing a specially designed 150KW plasma arc torch. A plasma arc torch is a device for producing an electrical "flame" called a plasma which is the hottest, sustainable flame known to man. The plasma arc torch takes a very small quantity of any gas (argon, hydrogen, helium, nitrogen, oxygen, air, etc) and, using electricity, changes this gas into a plasma flame. Unlike a combustion burner flame the plasma flame can be generated in the total absence of oxygen. Heat is, therefore, generated by electrical dissociation and ionization of the gas, which can be extensively exploited in many heating applications. The arc centreline temperature can be in excess of 10,000 deg C and the arc edge temperatures can be between 3,000 and 8,000 deg C. The torch is designed and built with no moving parts for trouble free performance and easy maintenance, and it can have an electrical to thermal conversion efficiency of over 90% depending on the size of the torch. When the plasma arc torch is operated as a self contained Plasma Heating System in a reactor vessel with the exclusion of oxygen the resultant processing of input materiel approaches pure pyrolysis.

Over the years a wealth of experience and knowledge has been gained with the plasma arc torch as the heat source for the processing of a wide range of input materiels. A major area of concentration has been in the processing of carbonaceous materiel in which pyrolysis provides for virtual complete gasification of all combustibles in the source materiel, while non combustibles are reduced to a virtually inert slag. The high process temperatures achieved by plasma processing ensure rapid and complete breakdown of chemical bonds and avoid the particulates and partially combusted hydrocarbons normally associated with combustion processes. Total gasification can, therefore, be achieved very efficiently. The general absence of oxygen results in significantly less air pollution from contaminants such as nitrous oxides (NOx) and sulphur dioxide (SO2) than is associated with conventional gasification processes.

The plasma arc processing of Municipal Solid Waste (MSW), with its high carbonaceous content, combines energy production with the destruction of a waste materiel with what is considered to be minimal environmental pollution. The characteristics of MSW gasification were developed a number of years ago through R&D work performed at the facilities of Plasma Energy Corporation (PEC) of Raleigh, North Carolina, with whom RCL has always been closely affiliated. The postulated 4-5 fold increase in usable output energy compared to input electrical energy represents a theoretical recovery of approximately 95% of the available energy in the input materiel, which together with the potential 300-350 BTU/scf product gas, the potential 20 to 1 volume reduction ratio of the silica metallic slag compared to the input MSW and the potential minimal requirement for environmental controls are very attractive process characteristics. This becomes even more attractive when considered with the design simplicity, low capital costs and operating versatility of a plasma arc gasification installation. However, prospective clients view these results as inconclusive since they were neither performed nor published in Canada, and there is no operational system in either Canada or the US which utilizes this technology in this application.

FEASIBILITY STUDY PROPOSAL

In an endeavour to authenticate these postulated characteristics and to increase the visibility and potential acceptability of the use of plasma technology in the gasification of MSW, RCL together with OBOE Engineering Limited of Ottawa and Ontario Hydro Research Division submitted an unsolicited proposal to the Ontario Ministry of Energy for consideration for funding of a feasibility study. The study was to be conducted in two stages, Stage 1 to determine the higher heating value of the product gas and the total process energy balance, and Stage 2 to determine the environmental acceptability of the process and the subsequent combustion of the product gas.

Stage 1 would concentrate on the determination of:

- the electrical power required to process a unit of input MSW;
- the volume of product gas generated from a unit of MSW input;
- the higher heating value (HHV) of the product gas compared to the HHV of the input MSW;
- the process heat losses;
- the potential commercial application for the output slag;
- the chemical composition of the output slag;
- the volume and weight ratios of output slag compared to input MSW; and

- the potential enthalpy of the product gas.

And then Stage 2 would concentrate on:

- analysis of the product gas for pollutants;
- analysis of the condensate extracted through drying of the product gas;
- analysis of the products of combustion of the product gas; and
- analysis of the resultant slag for pollutants.

Stage 1 was approved for a 1 April 1986 commencement with 52% of the estimated $252K cost being funded by the Ministries of Energy and Environment. The remainder of the Stage 1 funding will to be provided by the participants of the project and by Plasma Energy Corporation. Stage 2 will be reassessed for funding approval depending on the results obtained through Stage 1. The estimated cost of Stage 2 is $170K.

All experimental work is being performed in the RCL plasma research facility. The original facility, as depicted in Figure 1, required certain modifications in order for the required operational characteristics of such a process to be most accurately determined. The modified facility is depicted in Figure 2. Paramount among the changes were:

- the fabrication of a new reactor vessel complete with a hydraulic assisted feed system to better match the size of the existing plasma arc torch and to permit continuous feed throughout the full period of an experimental run;
- the addition of a condenser to dry the product gas to determine its maximum heating value;
- the addition of a blower system in the product gas line to draw the product gas to alleviate back pressure in the reactor vessel and hence alleviate materiel feed difficulties;
- the modification of the product gas cooler from a

bubble process to a spray process to improve the efficiency of the blower system; and
- the addition of a Gas Chromatograph to permit immediate readouts of the chemical composition of the product gas to ensure maximum accuracy.

Stage 2 will also require further modifications to the facility, however, only to the extent of providing a capability to store the product gas for later use in an extended combustion test. The combustion of this gas will be conducted in the existing boiler in the RCL plasma research facility.

THE EXPERIMENTAL PROCEDURE

MSW throughput in the 150KW plasma arc facility is estimated at 400-500 pounds per hour. Each experimental run will cover an eight hour period, therefore, upwards of two tons of MSW will be required per run. This MSW will be shredded, if shredded city refuse can be readily found, however, the facility could also accommodate "as received" city refuse provided no large objects are present. Standard garbage bags from residential streets could be handled very easily. The use of shredded garbage could more easily and probably more accurately permit ultimate and proximate analyses for comparison purposes. Steam can be introduced, as required, and at varying rates to provide additional free hydrogen to aid the process.

The control system is very versatile and enables one operator to process varying amounts of materiel from next to nothing to the maximum capability of the facility depending on the type of materiel being processed. The operator has continuous readout of:

- torch position within the reactor vessel;
- torch operating current and voltage;
- torch air input temperature and flow rate;

- torch coolant water input/output temperatures and flow rate;
- input materiel feed rate;
- process temperature within the reactor vessel;
- gas cooler/condenser input/output gas temperatures;
- gas cooler water input/output temperatures and flow rate; and
- reactor vessel pressure.

If certain of these parameters exceeds preset tolerance levels, the torch is automatically interlocked off.

The process temperature, as monitored at the inside wall of the reactor vessel, will be approximately 2000 deg F although varying temperatures will be tried in an endeavour to find the optimal temperature. The vessel will be preheated to this temperature prior to any processing being done. This preheating will be achieved through the use of a natural gas burner for the first 500 deg C, approximately, and then through the use of the plasma torch for the remainder.

Once the operating temperature is achieved, processing can commence. MSW will be weighed and then fed into the feed hopper. The feed hopper has two doors, one at the top and one between the hopper and the reactor vessel. The hopper will be filled with the inside door closed to retain heat in the vessel and to prevent the massive insertion of air. Once the hopper is full, the top door will be closed and the inside one will be opened to permit the MSW to be hydraulically fed into the vessel. The hydraulic system is adjustable to permit a variable rate of input materiel to be fed into the vessel. A plunger is also available to guard against blockages. The input materiels handler will maintain a specified level of MSW in the hopper to guard against the ingestion of large amounts of air into the process. With this specified level being maintained, the inside door can be left open for the full duration of the test. The pyrolysis operator will monitor the processing rate through the temperature sensor in the top of the vessel. An increasing temperature will indicate that the vessel is emptying and a lowering temperature will indicate that the MSW is being fed too rapidly. A sight window is also available so that the materiel level can be visually checked whenever needed. The Pyrolysis Operator will establish the optimum feed rate for the process. Varying the torch input power will cause a corresponding variation in the optimum feed rate.

Output slag will be permitted to accumulate in the bottom of the reactor vessel and will be removed through a trap door by hydraulically tipping the entire vessel. At a 20 to 1 volume reduction ratio between the input materiel and the output slag it is anticipated that a full experimental run can be conducted without the need for slag output. The slag will then be removed from the vessel at the end of each run in preparation for the next run.

The volume of product gas generated will be continuously recorded on a Bailey gas meter, which will be calibrated prior to the commencement of any experimentation, and a continuous log of all torch operating parameters will be maintained to facilitate full analyses at a later time. All other power usages through the process will also be monitored together with all process temperatures to facilitate the determination of heat transfer rates and the process heat balance. The product gas chemical composition will be monitored on a periodic basis to ensure a good cross sectional reading of the product gas quality. The product gas will be flared on exit since no further use of it will be required through Stage 1. The intent through the study will be to vary the operational parameters and monitor the resultant performance characteristics to determine the best operating characteristics. Figure 3 depicts the process energy balance considered achievable as derived from R&D conducted to date.

PRELIMINARY TESTING

Immediately preceeding the commencement of this feasibility study RCL conducted preliminary experimentation in the gasification of MSW for Plasma Energy Corporation. These tests were conducted in the original unmodified facility, therefore, obvious inefficiencies were present. Preliminary environmental analyses of the product gas was also conducted, as was preliminary chemical analyses of the resultant slag. The results obtained, although inconclusive due primarily to the lack of quantity of tests performed, indicated the feasibilty of the process and the potential achievability of the postulated characteristics. The analyses of the resultant slag, for example, strongly supported the claim that the slag is inert and non-leachable. This level of testing, however brief, proved very beneficial at the commencement of the current feasibility study in the determination of initial process parameters.

CURRENT STUDY STATUS

We are currently approximately two thirds of the way through Stage 1. We have effected all modifications to the facility and are now commencing operational testing. Nine operational tests are scheduled, after which the results will be fully analysed and a Stage 1 report will be prepared. It is anticipated that Stage 1 will be complete by approximately 1 March 1987. The results portrayed in the Stage 1 report will form the basis of a decision by the Ministries of Energy and Environment on whether or not to consider funding support for Stage 2.

BENEFITS/ADVANTAGES

The disposal of MSW is becoming an ever increasing problem for municipalities and environmental protection agencies alike. The standard age old disposal method of landfill is becoming increasingly less attractive as such sites are becoming full, alternate sites are becoming scarce and the knowledge and reality of contamination of adjacent facilities and property is becoming more prevalent and frightening. The alternative to landfill for MSW disposal has primarily been incineration in a number of forms. However, these forms of disposal have not been without their problems, from environmental to general public rejection on aesthetic grounds.

The success of this feasibility study to prove the postulated parameters of operation of plasma arc for the gasification of MSW could be extremely beneficial for this application, coming at a time when new and more environmentally acceptable solutions are sorely needed. This would not only open up a complete new application field for this emerging technology but it could be a significant boon to an ever increasing number of municipalities with existing city refuse problems. This would not merely be another way to get rid of MSW, but it could be a technological breakthrough with significant benefits.

The major benefits/advantages from this process could be:

- the standard output product of the plasma arc process is a producer gas which offers considerably more flexibility for use than, for example, sites which only produce steam;
- plasma arc gasifiers can have substantially lower capital costs since they can integrate more fully into a potential owner's existing facility, as compared to sites which require integral steam boilers thereby increasing the cost of these sites by 25 to 30%;
- the output energy of the plasma arc gasifier, being a producer gas, can be stored for future use similar to natural gas, as compared to steam boiler installations where the energy is lost if it is not used virtually immediately;
- the operating temperature and the heat transfer rate of

the plasma arc process can be variable, relatively at will, therefore, the optimum operating temperature and rate of reaction can be achieved, varied and maintained to minimize undesirable output pollution products and maximize the energy recovered from the input materiel;

- the plasma arc gasification process does not depend on the combustion of any of the input materiel for the pyrolysis process, therefore, the quantity of output energy produced per unit of input materiel can be maximized;
- plasma torches have the potential to deliver the heat of reaction much faster than conventional heat sources enabling the complete breakdown of the input materiel and the production of smaller molecules which are inherently less hazardous;
- the ability to process materiel at any rate from next to nothing up to the maximum capacity of the facility and still operate at the optimal operating point is a very desirable feature;
- the fact that the materiel enters into two chemical reactions, once during the pyrolysis process for the generation of the product gas, and once during the product gas combustion process, before any by-products are exhausted to the atmosphere ensures minimization of pollutants;
- metallics and glass in the input materiel melt, thus substantially reducing the volume of the output slag and alleviating problems with its disposal; and
- there is a potential commercial market for the slag produced through plasma arc gasification of MSW thereby virtually eliminating the requirement for continued operation of controlled landfill sites for MSW.

DISADVANTAGE

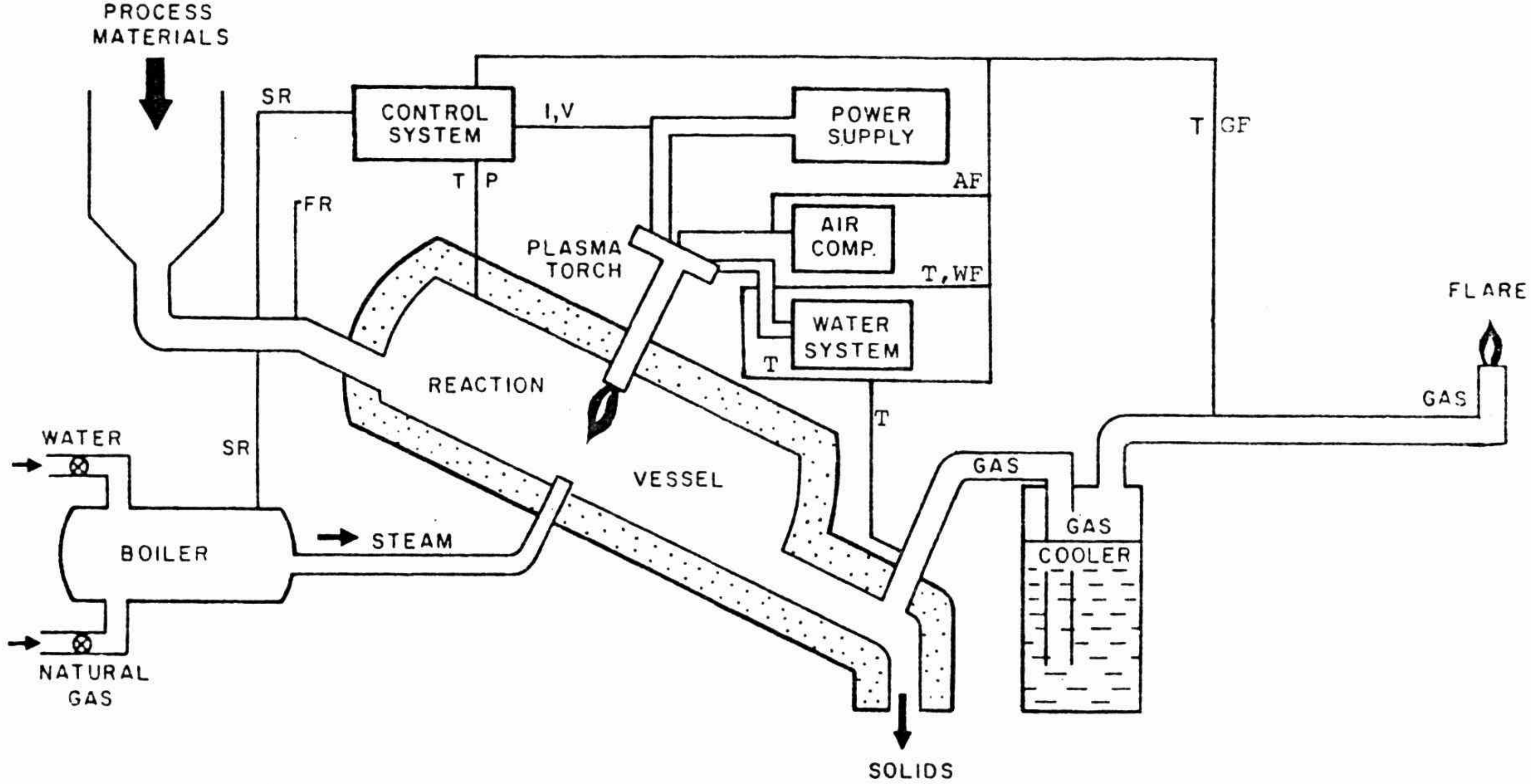
The primary disadvantage in this process is the operating costs associated with the high electrical consumption. This cost is somewhat offset by the higher volume of product gas generated and, in some cases, it can be further alleviated by operation at lower power during peak hydro usage periods. For example, demand charges can be from 30%-90% lower, depending on the hydro district, for operation between 8PM and 8AM and all day Saturday and Sunday, which potentially can be used to advantage. The extent of this advantage would be dependent on the design and operational characteristics required of the installation.

CONCLUSION

The participants in this feasibility study remain very optimistic that the experimentation will be highly successful and the plasma gasification of Municipal Solid Waste will become a fact of the future.

RESORPTION
CANADA LIMITED

FIGURE 1 - PLASMA RESEARCH FACILITY - ORIGINAL



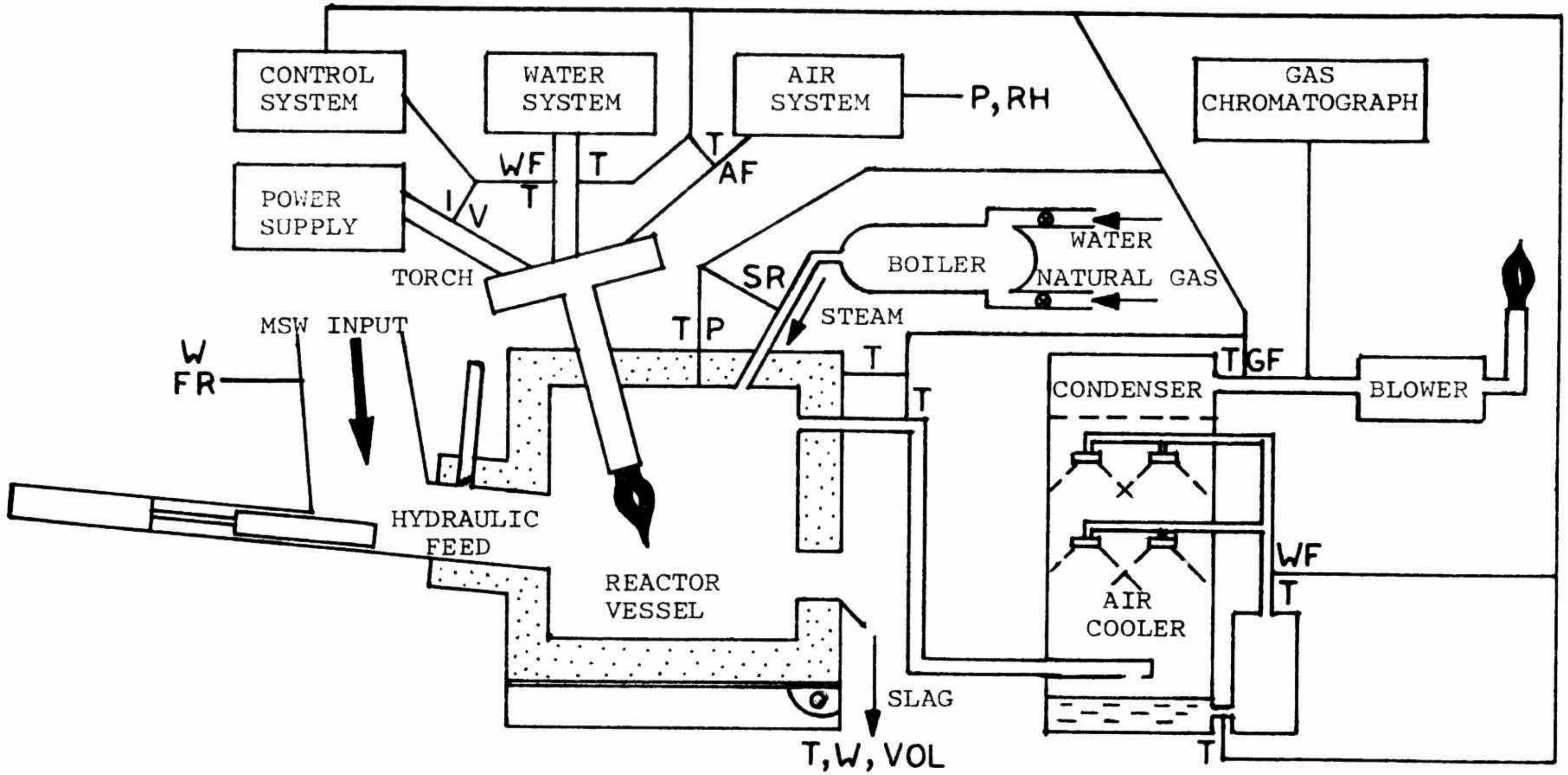
I - CURRENT (AMPS) V - VOLTAGE (V) T - TEMPERATURE (DEGREES C)

FR - MAT'L FEED RATE (LBS/HR) SR - STEAM RATE (LBS/HR) P - PRESSURE (PSIG)

AF - AIR FLOW RATE (CFM) WF - WATER FLOW RATE (GPM) GF - PRODUCT GAS FLOW RATE (SCFH)

RESORPTION
CANADA LIMITED

FIGURE 2 - PLASMA RESEARCH FACILITY - MODIFIED

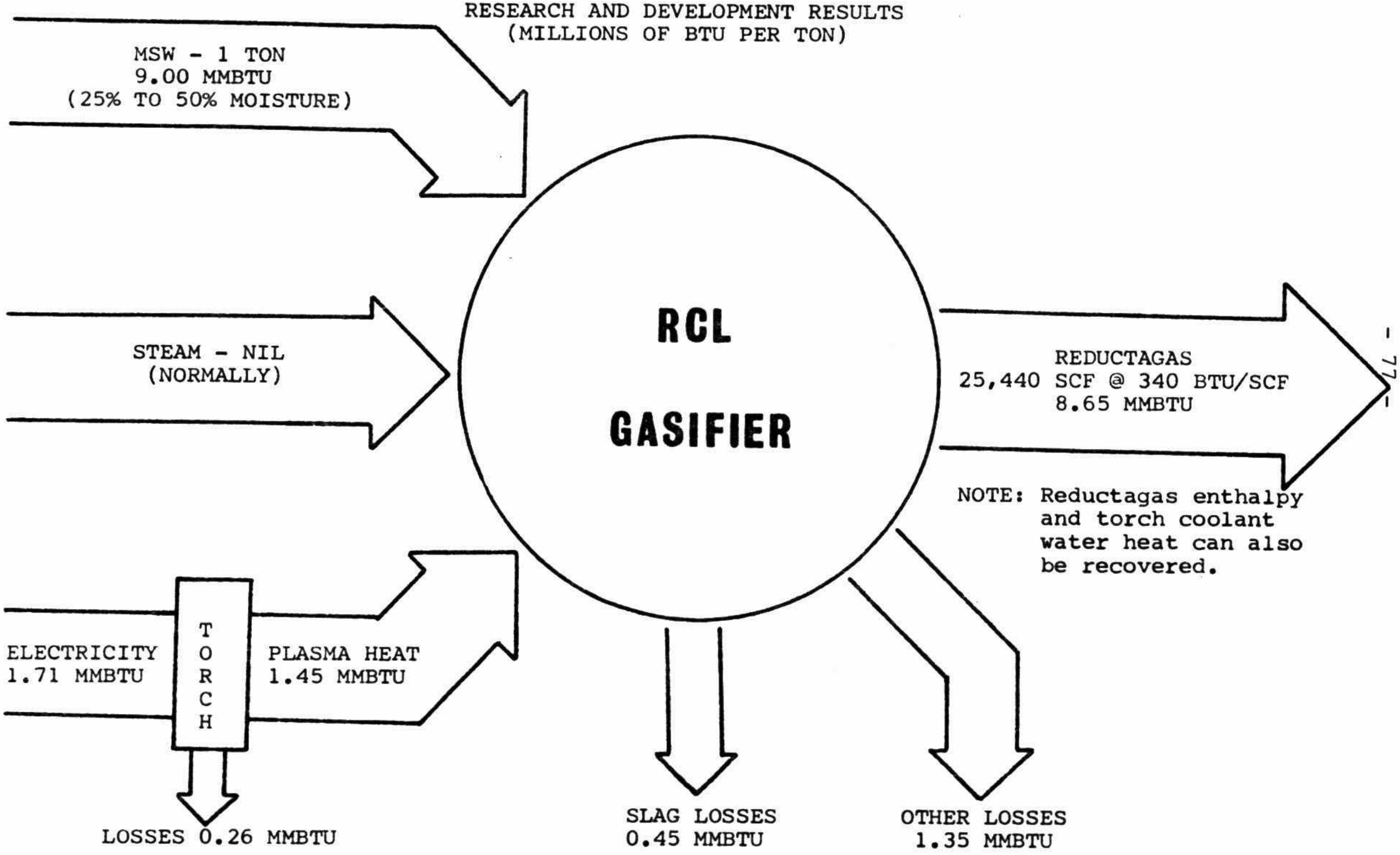


I - CURRENT (AMPS)
V - VOLTAGE (VOLTS)
T - TEMPERATURE (DEGREES C)
FR - MAT'L FEED RATE (LBS/HR)
SR - STEAM RATE (LBS/HR)
P - PRESSURE (PSIG)
AF - AIR FLOW RATE (CFM)
WF - WATER FLOW RATE (GPM)
GF - GAS FLOW RATE (SCFH)
RH - RELATIVE HUMIDITY (%)
W - WEIGHT (LBS)
VOL - VOLUME (CF)

FIGURE 3 - **RESORPTION CANADA LIMITED**

MUNICIPAL SOLID WASTE GASIFICATION YIELDS

RESEARCH AND DEVELOPMENT RESULTS
(MILLIONS OF BTU PER TON)



NOTE: Reductagas enthalpy and torch coolant water heat can also be recovered.

SEWAGE SLUDGE COMPOST AS TURF FERTILIZER

J.L. Eggens, N.L. Pierce, and C.P.M. Wright

University of Guelph
Guelph, Ontario

SEWAGE SLUDGE COMPOST AS TURF FERTILIZER

Eggens, J.L., N.L. Pierce and C.P.M. Wright
Department of Horticultural Science,
University of Guelph,
Guelph, Ontario, N1G 2W1

Abstract. The suitability of the Windsor composted sludge for turf was evaluated on home lawn-type turf (primarily *Poa pratensis* L.) at the Horticultural Research Station at Cambridge and on mixed *Poa annua* L. and *Agrostis palustris* Huds. turf at the Weston Golf and Country Club, Weston, Ontario. At both locations, turf fertilized with the Windsor material was as similar to turf fertilized with urea. At the Cambridge site, the turf treated with the Windsor material (+urea) was similar to that treated with Milorganite. There appeared to be no difference in thatching tendency, susceptibility to drought or disease, in turf color or turf growth. On the golf course turf, the speckling commonly noted with urea was not evident with the Windsor material. A *Poa annua* L. sward has been established at the Cambridge site to evaluate the response of this species to the Windsor material and Milorganite during 1987.

Sewage sludge composts produced by the Beltsville Aerated pile method has been used successfully in the growing media of various non-edible horticultural crops: bedding plants (Chaney, *et al.*, 1980), container-grown woody ornamentals (Sanderson, 1980) and nursery sod production (Murray, 1981). Eggens (1982) found that composted sewage sludge was as effective as sphagnum moss peat as an organic amendent for turf rootzones receiving compaction stress.

Annual bluegrass (*Poa annua* L.) is a major component to turfs on athletic fields, lawn bowling greens and golf courses in Ontario. While it is generally considered to be a major grass weed, cultural and chemical weed control practices have been relatively ineffective in preventing its invasion into and dominance of high maintenance turf swards. Because of the extensiveness of annual bluegrass in these turf areas, turf managers have attempted to maintain it somewhat as a permanent turf cover. The results from Waddington, *et al.*, (1978) and Engle and Bussey (1979) suggests that annual bluegrass is less competitive with creeping bentgrass on putting greens when the nitrogen is from an inorganic source such as urea or a synthetic organic source such as Ureaformaldehyde than when the nitrogen source is an organic fertilizer such as Milorganite. While some researchers have attempted to relate phosphorus (Waddington, *et al.*, 1978) and micronutrients (Morgan, 1982) to this response, the reasons for this response is not well understood.

The objective of this research is to determine the suitability of the Windsor composted sewage sludge as a general turf ferilizer and compare the response of annual bluegrass to the Windsor composted sludge and Milorganite.

Materials and Methods

A preliminary study (Financed by the City of Windsor) on the Windsor composted sludge was conducted on a Kentucky bluegrass-red fescue turf on the University of Guelph campus during the summer of 1984. The turf received medium management (as a home lawn) with irrigation as required to prevent drought stress. Milorganite and Windsor composted sludge was applied (4 replications) at 0, 100, 200, 300 and 400 kg ha^{-1} every 2 weeks from June to October (8 applications).

The second study (started October 1985) was conducted at the Horticultural Research Station, Cambridge, Ontario, on a 5-year-old mixed Kentucky bluegrass, annual bluegrass, red fescue, creeping bentgrass turf. The turf received medium management and irrigated as required to prevent drought stress. Nitrogen from Urea, Milorganite, and Windsor composted sludge (+urea) was applied 8 times from April to October to supply 0, 100, 200, 400 and 800 kg N ha^{-1} over the growing season. The Windsor compost and Milorganite were applied at equal rates of product.

The third study (started July 1986) was conducted on a high maintenance putting green nursery turf mowed at 9 mm, 3 times per week and irrigated regularly. The sward consisted of approximately 70% Penncross creeping bentgrass and 30% annual bluegrass. Phosphorus and potassium were supplied according to soil test. Nitrogen was supplied as Urea or Windsor sludge compost at 0, 12 and 25 kg N ha^{-1} every two weeks.

For the 3 studies the turf response to treatment was evaluated visually using a scale of 0 to 10, 0 equalling zero or dead turf and 10 equalling ideal turf. The plots were evaluated for color, density, disease and injury from stress.

Results and Discussion

When the Windsor sludge compost or Milorganite was applied to a mixed turf on the University of Guelph campus the milorganite plots generally scored higher for green color than the Windsor compost. Milorganite had 6% N while the Windsor compost was approximately 1% N. However, after about 6 applications of equal amount of product, fertilizer burn patches appeared on the Milorganite treated turf (Table 1). Similar injury did not appear on the Windsor treated turf.

Table 1. The effect of nitrogen source and product application rate on a mixed turf on the University of Guelph Campus (September 1984)

N Source	Control	Injury (% of plot) 1 kg	2 kg	3 kg	4 kg
Windsor	0 a^z	0 a	0 a	0 a	0 a
Milorganite	0 a	30 b	33 b	20 b	23 b

^{z}a-b means followed by the same letter are not significantly different = 0.05 (DMRT).

In the second study at the Horticultural Research Station the turf on plots treated with Urea, Milorganite and Windsor compost (+urea) were similar at all N rates (Table 2). The color of the turf became darker green as the nitrogen rates increased. The time period involved was too short to result in any observable change in the botanical composition of the sward, thatch accumulation, stress susceptibility or proneness to disease. This study will continue for several years.

Table 2. The effect^{y} of nitrogen source on a mixed turf at the Cambridge Research Station.

N source	N rate (kg ha^{-1})	1985	1986					
		Oct 23	Apr 18	May 19	June 20	July 22	Aug 6	Sept 15
Control	0	7.0^{z}	6.8a	6.9a	6.3ab	6.2a	6.5ab	6.5ab
Windsor	100	6.5a	6.5a	6.5a	6.0a	6.8b	6.5ab	6.5ab
Windsor	200	7.0a	7.3a	6.3a	6.5ab	6.8b	6.8ab	6.5a
Windsor	400	6.8a	7.0a	6.8a	7.0b	7.8c	7.3b	7.8c
Windsor	800	7.5a	7.3a	7.3a	8.0c	7.8c	7.8c	8.8c
Milorganite	100	7.0a	6.8a	6.3a	6.3ab	6.8a	6.5ab	6.5a
Milorganite	200	7.0a	6.5a	6.5a	6.3ab	7.0b	6.8ab	7.0b
Milorganite	400	6.5a	6.3a	6.8a	6.8ab	7.0b	7.0b	7.3b
Milorganite	800	7.5a	7.3a	6.8a	7.8c	7.8c	7.8c	8.0c
Urea	100	7.3a	5.8a	7.0a	6.8ab	6.8a	6.5ab	6.8ab
Urea	200	6.5a	6.3a	6.8a	6.5ab	6.5a	6.8ab	6.3a
Urea	400	7.0a	6.0a	7.0a	6.8ab	7.0b	7.3b	8.0c
Urea	800	7.3a	7.0a	7.0a	6.8ab	7.0b	7.8c	7.8c

[z] a-c means followed by the same letter are not significantly different P = 0.05 (DMRT).

[y] Visual observation on a scale of 0 to 10, with 0 equalling dead turf and 10 equalling dense, dark green turf.

Table 3. The effect[y] or nitrogen source on a Penncross annual bluegrass putting green nursery turf (July to Sept).

N source	N rate (kg ha^{-1})	July 24	Aug 8	Sept 5
Control	0	6.3a[z]	7.0a	7.0a
Windsor	12	8.7b	9.3b	7.7b
Windsor	25	9.3b	9.3b	8.0b
Urea	12	9.0b	8.3b	8.0b
Urea	25	10.0b	9.7b	7.7a

[z] a-b means followed by the same letter are not significantly different P = 0.05 (DMRT).

[y] Visual evaluation using a rating system of 0-10 with 0 representing dead turf and 10 ideal turf.

In the third study on a Penncross creeping bentgrass nursery, the turf on plots receiving the Windsor compost and urea were similar. No injury was observed on the Windsor compost plots. Some "speckling" injury, common on turf treated with urea, began to appear on 5 Sept 86. The time period involved was too short to result in any other observable differences.

Conclusion

The studies reported here were of very short duration, too short in fact, to make any specific conclusions. One observation is valid however. When applied at high rates Milorganite had a very objectionable odor while no observable odor was noted from the same high rates of the Windsor sludge compost.

Literature cited

Chaney, R.L., J.B. Munns and H.M. Cathey. 1980. Effectiveness of digested sludge compost in supplying nutrients for soilless potting media. J. Amer. Soc. Hort. Sci. 105:485-492.

Eggens, J.L. and C.P.M. Wright. 1982. Composted urban waste as a soil amendment for turf. Can. Hort. Council.

Engle, R.E. and C.W. Bussey. 1979. The effect of fertilization on annual bluegrass. Golf Course Management. Sept/Oct:40:42.

Morgan, W.C. 1982. Iron nutrition of turfgrasses. J. Plant Nutrition 5:955-959.

Murray, J.J. 1981. Utilization of composted sewage sludge in sod production. Proc. 4th International Turfgrass Research Conference Guelph. 544.

Sanderson, K.C. 1980. Use of sewage-refuse compost in the production of ornamental plants. HortScience 15:173-178.

Waddington, D.V., T.R. Turner, J.M. Duick and E.L. Moberg. 1978. Effect of fertilization on Penncross creeping bentgrass. Agron. J. 70:713-718.

WASTE MANAGEMENT PLANNING FOR PHARMACEUTICAL INDUSTRY -- PHASE I, INVENTORY AND DATA COLLECTION

Ramesh Makhija and Robert A. Stairs
Department of Chemistry
Trent University
Peterborough, Ontario
K9J 7B8

Introduction

The pharmaceutical manufacturing industry is a complex one. A great many chemical substances are used in relatively small quantities. The grouping of products in this industry is much more a function of the uses of the formulations to treat specific types of diseases than of their chemical nature or kind of hazards they may represent. The formulator must be concerned with meeting strict standards on toxicity, long-term stability, taste, odour, solubility and appearance. One would expect a high fraction of wastage in consequence. In fact, the reverse is true; such close control is exercised on the purity of raw materials and at each stage in the processing and packaging that wastage is minimal, and, as will be shown, the quantities of wastes produced are small.

The first phase of this study has been concerned with data collection for an inventory of types and quantities of wastes produced, and their present modes of disposal, as reported by the manufacturers themselves and by certain major users. The objectives to be achieved in this phase were:

(a) To estimate the types and quantities of wastes;

(b) To determine present disposal practices (and incidentally to estimate the costs of disposal;

(c) To identify hazardous waste streams or classes of liquid or solid wastes which might qualify under Regulation 309 as hazardous.

Methodology

A questionnaire had been prepared by the Ministry of the Environment, which we obtained in late 1985 and used as the basis of a considerably modified one. This we sent in January of this year to about 70 manufacturers and institutions. We have received replies from 35 establishments, including 6 hospitals. The others we have tried to elicit replies from by follow-up letters and repeated telephone calls, without success. Our original list was longer, but a number of firms have either closed or ceased manufacturing operations. Table 1 lists the responding manufacturers, and their chief products. We understand that the Ministry will approach non-respondents shortly, to encourage their participation.

The list of recipients of the questionnaire included nearly all the leading pharmaceutical manufacturers in the Province of Ontario, plus three large hospitals in Toronto, two smaller ones in Peterborough, and one each in Campbellford, Lindsay and Port Hope, and a few distributors and repackagers. We are pleased with the response; a 50% return from a mailed questionnaire is a fair return. We are grateful to the managers and employees of those establishments that took the trouble to reply to our questionnaire, and especially to the three firms, Connaught Laboratories in Toronto, Pfizer in London and Johnson & Johnson in Guelph, and to Toronto General Hospital, who invited us to visit them to clarify the purpose and significance of our questionnaire, and to enable us to explain to them our objectives, and to explain also the relevance of Regulation 309 to our study and to their operations.

The questionnaire is reproduced below as Appendix A. It divided the products of the industry into eleven categories, by end use. For each category the respondent was asked for answers to four questions: typical quantity disposed of annually, whether any are "Liquid Industrial Wastes", method of disposal and annual disposal costs. Twenty-two other questions are asked most of which require only "Yes" or "No" answers. They cover information about the company and its products, and certain aspects of company policy and practice with respect to waste management.

Results

A summary of the responses received forms Table 2, in the same format that was used in the questionnaire. As may be seen from the Table, the total quantity reported of all wastes is not large, being only a little under 250. tonnes, or assuming that the non-respondents will eventually produce similar figures, 500 tonnes in all. This is a minute fraction of the annual chemical waste disposal total for Ontario.

It is not clear from the Table, but our preliminary findings suggest that, in general, good disposal practices are being followed. Much material is incinerated, and we have no reason to believe that the residues that go to landfill pose any hazard. The only doubtful practice we have come across is that certain materials are going into municipal sewers that may cause concern unless they can be shown to be biodegradable or in some way detoxified, or both. This is being looked into.

It became apparent as the results of the questionnaire were analysed that additional information was required on two points. The questions on quantity of material disposed of elicited answers that were inconsistent, in that some respondents reported the net quantities of active ingredients, while others reported gross quantities. Telephone inquiry has cleared up this difficulty in large part. The quantities reported here are gross. The second matter relates to substances other than actual pharmaceuticals, i.e., solvents, raw materials and intermediates, which were not mentioned at all. We think they should have been, and we will seek this information in follow-up inquiries.

We suspect that solvents, in particular, may prove to be an important item. Local inquiry at three hospitals has shown that quantities of solvents worth recovery and recycling are being removed by licensed carriers. One company volunteered the information that their quality control and research laboratories generated quantities of waste solvents that cost them $5,000 for disposal. There must be many companies with similar experience. If an economic system of collection and recycling can be devised, we believe that large savings may be possible. The assistance of Government or of the Ontario Waste Management Corporation may prove to be valuable.

There were very few wastes reported that are subject to Regulation 309, though a number of companies commented that small amounts of such wastes were generated, below the exemption limits. The chief exception was one report of 190,000 L of liquid industrial waste, under our category of mineral-based pharmaceuticals. At the time of writing, the Ministry's records are being searched for items reported under the Regulation.

The costs reported do not appear to be enormous. We arrived at a total of $93,700 for the 36 companies for a year, and again assuming non-responders have similar experiences, estimate a total cost for the Ontario industry of about

$180,000. This is probably not a significant fraction of the cost of doing business. Nevertheless, in certain cases economies are probably possible.

Response to Survey Questions

The twenty-three numbered questions in the questionnaire include some that are of an administrative nature, but the answers to questions that are significant in this study are summarized in Table 3. In this table, (and in Table 2) it will be noted that columns do not always add up to the noted totals, or correspond to the total number of firms replying. In most cases this is due to overlapping categories of reply, but some of the replies were somewhat confusing, and uncertain replies may have been counted in two ways. These points will be clarified where possible.

Significant aspects of the replies will be noted. Several firms mention solvent waste streams, few of which are being recycled or recovered. Only half the replying firms actually manufacture in Ontario; the rest are formulators, repackagers or distributors only. Of the actual manufacturers, 70% are in the Totonto area. The business of waste disposal is rather concentrated; one firm handles 30% of the hauling and 44% of the receiving (excluding landfill).

Corporate responsibility, or at least awareness, in this field seems good. Most of the firms report the use of waybills (presumably all that dispose of significant amounts of hazardous substances); most have explicit policies and guidelines on disposal of toxic substances. Waste reduction, treatment and recovery are subject to economic dictates. The small number of firms reporting treatment or recovery on site probably reflects the high capital cost of facilities for these purposes. Several firms report off-site recovery of solvents, in particular. (This question was not asked.) Half the firms report waste-reduction incentive schemes or other encouragement. The majority of the others are not significant generators of wastes.

Conclusions

The present report is preliminary, and is to be amplified and compared with experience in other jurisdictions, and (as noted above) with other information from Ministry files. It may already be noted, however, that the problems associated with waste disposal in the pharmaceutical industry are not severe, either in environmental or in economic terms. The only recommendation we are in a position to make is that already mentioned, that more effort should be made to encourage recovery and suitable recycling of solvents. It may not always be possible to restore solvents to the degree of purity required by the original user, but other users may have less stringent requirements. Where quantities justify the capital expense, the most convenient way is in-house recycling, but externally contracted recycling is immediately available from at least one firm.

Acknowledgements

The continued assistance of the Waste Management Branch, and a generous grant from the Ministry of the Environment of Ontario are gratefully acknowledged.

TABLE 1

Major producers of pharmaceuticals in Ontario

	analgesics	antihistamines	antitussives & expectorants	sedatives and anticonvulsants	psychotherapeutics	cardiovascular agents	corticosteroids	estrogens	antibiotics
Allen & Hanburys	x			x		x	x	x	x
Ames/Dome/Miles	x						x		x
Anca Laboratories	x			x		x			
Astra Chemicals						x			
Denver Laboratories					x				
Dow Pharmaceuticals	x	x	x		x				x
Drug Trading	x			x	x	x	x		x
Fisions (Canada)	x		x						x
Fulford Dodds	x								
Glaxo Laboratories							x		x
Lilly, Eli & Co.	x	x		x	x		x		x
McNeil Laboratories	x			x	x				
Mead Johnson	x					x		x	
Merrell, William S.								x	x
Norwich Pharmacal Co.	x								
Novopharm Ltd.	x	x		x	x	x	x		x
Organon Canada							x		
Ortho Pharmaceutical								x	x
Parke Davis & Co.	x	x	x	x		x	x	x	x
Paul Maney Laboratories				x	x				x
Pennwalt of Canada			x						
Pfizer Co.					x		x		x
Purdue Frederick Co.	x					x			
Riker Pharmaceutical Co.	x		x						x
Rorer, William H.	x				x				
Searle Pharmaceuticals				x				x	
Sterling/Winthrop	x		x	x		x			x
Upjohn Co. of Canada	x		x				x	x	x
Wampole Ltd.	x								
Warner-Chilcott	x			x		x	x		x
Whitehall Laboratories	x								
Wyeth Ltd.			x	x		x		x	x

TABLE 2

Class of Pharmaceuticals	No. of Respondents	Quantity Disposed of Annually Kilograms or Litres	Hazardous or "liquid industrial" waste (Regulation 309)	Present Method of Disposal Incineration (I) Landfill (L) Mun. Sewer (S)	Estimated Cost for Disposal Annually $(000)
Antihistamines	7	250	---	L or I	1.3
Antitussives, sedatives, anticonvulsants, anaesthetics and analgesics	8	3,100	1 (Thiamylal-Sodium) controlled drug	L/I	2.5
Psychotherapeutics	5	1,400	---	L/I	4.0
Cardiovascular agents	7	2,000	---	L/I/S	1.5
Corticosteroids	7	410	2	L/I/S	1.7
Hormones & synthetic substitutes, including estrogens	8	12	---	L/I/S	---
Anti-infective agents, including antibiotics	9	254	---	L/I/S	2.61
Biologicals, including vaccines	6	18,300	---	I/S	40.1
Antineoplastics	3	70	---	I/L	0.3
Organic-based pharmaceuticals, not otherwise specified	9	26,400	---	I/L/S	7.2
Mineral-based pharmaceuticals, not otherwise specified	2	190,000	Industrial liquid waste	I/L/S	12.1
Category not specified	3	25	---	I/S	20.4
TOTALS	36	242,221	---	---	93.7

TABLE 3

Summary of Replies to Numbered Questions

Question No.	Topic		No. Reported
6	Major hazardous waste streams		
	Solvents: halogenated		3
	non-halogenated		3
	miscellaneous		3
	Chemicals: miscellaneous		2
	rejected pharmaceuticals		2
	Pathological		1
7	Number of plants		17
8	Location of plants		
	Toronto area		12
	Belleville		2
	Aliston		1
	Lindsay		1
	Perth		1
9	Haulers		
	Firm A*	used by -	7
	B		4
	C		3
	D		2
	Seven others	(one each)	7
10	Receivers		
	Municipal or other MOE approved landfill		9
	Firm A		10
	Firm C		4
	Firm E		2
	Seven others	(one each)	7
11	Waybills used?		
	Yes		20
	No		6
12	Corporate waste disposal policy?		
	Yes		22
	No		1
13	Guidelines on disposal of toxics?		
	External		14
	Internal		10
	None (or no reply)		7
17	Waste reduction procedures used?		
	Yes		10
	No		12
	N/A		17

Table 3, page 2.

Question No.	Topic	No. Reported
18	On-site waste treatment?	
	Yes	2
	No	22
	N/A	14
19	On-site recovery or recycling?	
	Yes	3
	No	17
20	Waste-reduction incentives?	
	Yes	16
	No	7
	N/A	16

*Firm names on file with Ministry of the Environment, as Appendix B to this Report.

"Development of Guidelines for the Utilization of Industrial Waste in Backfill and Construction Applications",

G. Zukovs,
Canviro Consultants Ltd.
Toronto, Ontario

This paper will be distributed at the Conference.

Numerical and Laboratory Modelling of Two-Phase Flow in Porous Media: I. Two-Phase Gaseous Flow. II. Two-Phase Liquid Flow

by

G.J. Farquhar, E.A. McBean, J.M. Byrne, W. Abbott,
R. Kell and B. Stickney
Department of Civil Engineering, University of Waterloo
Waterloo, Ontario, N2L 3G1

Abstract

Numerical and laboratory modelling of two-phase fluid flow in porous media is taking place under a larger project "Assessing the Impact of Hazardous Liquids Spilled Onto Soil". Numerical models to simulate two-phase liquid and vapour situations have been developed, and early verification against laboratory data has produced very good results. Liquid phase experiments are monitoring the migration of an immiscible liquid through a 60 cm. water-saturated vertical sand column. Relative liquid saturation behind the intruding front is monitored to steady-state with the thermal conductivity probe developed at the University of Waterloo. Relative permeability curves as a function of oil and water relative saturations have been developed.

Two phase gaseous flows are being modelled in a flux chamber. Hexane as a liquid is introduced in a pan and allowed to volatilize and migrate away from the source. Numerical and laboratory results are compared to determine soil absorption properties and variabilities in the parameters governing hazardous diffusion in porous media.

Research on the behavior of hazardous immiscible liquids (HIL's) in soil supported by the Ontario Ministry of the Environment has been in progress since January, 1984. This paper provides a general review of the project accomplishments to date as well as some results from recent experiments on the movement of HIL's and their vapours in soil.

GENERAL REVIEW

1.0 Modelling

1.1 Spill Propagation Models

Spill propagation models were developed to aid in understanding how spills of HIL's form, move outward and penetrate the soil. They were also designed to assist with spill remediation by providing a rapid simulation of the lateral and vertical spreading of the liquid. In this regard, the work has made an important contribution to the science of HIL spill management, providing the first models of their kind for HIL's.

Wall Model

The Wall Model (Wall, 1984) for spill propagation is based on the St. Venant equations for liquid flow in 2-D axis-symmetrical co-ordinates. It includes components which simulate evaporation and infiltration from a growing pool of spilled HIL and is able to conserve both mass and momentum. The equations are solved by approximate numerical methods in a computer code. Spill experiments were performed in part to permit model verification. Model simulations of the experimental data were reasonably good although the model did not handle as well as expected, the differences in contact angles between HIL's and the spill surface. The model, while quite accurate in its simulations, is rather expensive to use. Consequently, a second model was developed.

MBPF Model

The MBPF Model for spill propagation is an empirical model based on the work of Raisbeck and Mohtadi (1974). It was adjusted to accommodate; spill surfaces at various angles, variations in the contact angle between the HIL and the surface, evaporation, and infiltration. Both laboratory and field experiments provided a basis for testing the model. The model was able to simulate the experimental data quite well.

1.2 Liquid Penetration Model

The Osborne-Sykes Model (Osborne, 1984) for penetration of HIL's through soil was developed and tested during this research programme. The model solves the partial differential equations describing intergranular porous media flow equations (Bear, 1970) adjusted to handle immiscible liquids. The equations are solved in 2-D by means of a finite element method computer code.

The model was subsequently used to simulate the results of laboratory scale experiments on the movement of HIL's in soil columns. The experiments are described below. The simulations performed did not fit the data particularly well (predicted velocities were twice that of measured values). This was attributed in part to the hydraulic conductivity and capillary pressure versus saturation data used as input for the model. Actual data for the HIL's used were not available and thus substitutes were used. Experiments are now in progress in order to provide such data for the specific liquids used. Since the simulations generated were of the correct form and magnitude, it is felt that the model performs well.

The availability of the Osborne-Sykes Model is a significant contribution to solution of HIL spill problems. It can provide useful estimates of how a spilled liquid will behave in the soil; how deeply it will penetrate, how it will behave at the zone of saturation and what will occur if the liquid peentrates the zone. Such information would be most helpful in the design of remedial measures at the site and in assessing the severity of the problem.

1.3 Vapour Transport Model

The Allan Model (Allan, 1986) was developed to simulate the movement of vapours from HIL's in soil, a problem of growing concern at spill sites. The model is a 2-D finite element solution to a system of intergranular porous media flow partial differential equations. It is based on a landfill gas migration model developed previously under NSERC sponsorship. It has been tested against field data and the results from a limited number of laboratory scale experiments to be described subsequently. The comparisons between the two have been excellent.

The value provided by the Allan Model lies in its capacity to simulate the extent of suspected problems and to evaluate the success of vent or barrier control methods. It may also be of use in helping to track the movement of the actual liquids themselves.

2. Experimentation

Experimentation was performed with several objectives in mind; to provide information about the movement and retention of HIL's onto and into soil under both laboratory and field conditions, to produce a data base for use in calibrating the models developed in the work, and to develop experimental methods and equipment suitable for the study of HIL and vapour movement in soil.

2.1 Spills

Laboratory: Small Scale

Ethylene glycol and hexane as examples of HIL's were spilled from various heights through a 2.0 cm orifice onto an impervious surface either flat or inclined and either smooth or rough. Liquid volumes up to 5 litres were used. Video cameras were used to collect time dependent data on spill diameter, depth, hydraulic jump location and flow rate (source liquid height). The spill propagation models, as mentioned above, were then used to simulate the spill for the specific conditions of liquid viscosity, mass density, contact angle, discharge height and flow, and surface roughness and inclination.

Field Scale

Large scale spills were carried out in co-operation with the firm of S.L. Ross in Ottawa using both impermeable and sodded soil surfaces, either flat or inclined at 10°. Up to 200 L of liquids with viscosities ranging from 1 to 65 cp were spilled onto the various surfaces at rates ranging from 22 to 95 $\ell .\mathrm{min}^{-1}$. A total of 27 experiments were completed. The data recorded with respect to time included bore and hydraulic jump locations, depths, runoff and infiltration.

The spills were simulated using the MBPF model with good fits produced. The model roughness coefficient (n) was used as a fitting parameter with values ranging from 0.005 for a painted surface to 1.75 for a sodded surface.

Both sets of spill experiments provided useful quantitative data about the spreading and infiltration of HIL spills in response to variations in fluid type, spill rate and receptor surface slope, roughness and permeability. Similar data from other sources were extremely limited prior to this work. The experiments also provided a data base from which spill models could be developed and tested.

2.2 Liquid - Soil Interactions

Penetration Experiments

Experiments were, and are being performed in laboratory scale columns (7.3 cm diam. x 61.1 cm long) with HIL's being allowed to pass through sandy soil under continuous flow conditions. Liquids including oils, hexane, decane and perchlorethylene, are loaded to the columns at various flow rates and antecendent soil water contents. Measurements are made to determine the rate of movement of the HIL into the soil. Important information on transport velocities as influenced by liquid viscosity, density and contact angle and soil moisture and permeability has been obtained. Very little similar information was available prior to this work. It has provided insight into the nature of HIL movement through soil as a result of a spill. It has also provided a useful data base from which model evaluation can be made. This was, in fact, done for for the Osborne/Sykes Model. As noted previously, however, the model simulations were only fair because of limitations in the input hydraulic conductivity and capillary pressure data. Some recent results are presented subsequently.

Storage and Leaching of HIL's in the Unsaturated Zone

Experiments are being carried out in soil columns to determine the short- and long-term ground water contamination potential from a spilled HIL held in the vadose zone. Soil columns at various antecendent moisture levels are subjected to large volume oil spills. The oil is allowed to diffuse through the soil profile for a period of days. Effluent is collected, and the relative volumes of oil and water are determined with a centrifuge. Once the profile has stabilized (i.e. no further drainage of oil or water), pulse "rainfall" treatments are introduced at three day intervals. These data are being utilized to develop time and mass dependent contaminant removal curves.

The experiments, though begun only recently, have already provided significant insight regarding the residual HIL storage in the vadose zone as related to antecedent soil mositure conditions at the spill site. One anticipated recommendation will address immediate data collection of site soil mositure conditions by the spill response team. These data will allow accurate predictions of the HIL quantity remaining in the vadose zone, and estimation of the rate of contaminant leaching by infiltrating precipitation.

Several other liquids, including hexane, heptane, perchlorethylene and cyclohexane, are under consideration for use in this experiment.

Detection Methods

Detecting the movement of a HIL as it displaces the native soil fluid at a point, proved to be a challenge in this research. Methods based on polarity and dielective constant differences between the fluids were tried but proved difficult to use. Finally, a thermal conductivity probe was devised consisting of a heating coil surrounding a thermocouple with a total diameter of 3 mm and a length of 12 cm. A predetermined amount of current is passed through the probe for a fixed time and the rise in temperature as a function of fluid thermal conductivity is measured. The reproducability of the probe response is excellent. Subsequent experiments to detect the passage of a HIL through water-wetted soil have given very good results. The development of this probe has enabled non-destructive experiments to be conducted on continuous HIL flow in porous media. This is a major achievement. Work to develop the probe into a unit for the detection of HIL movement in the field is planned.

2.3 Vapour in Soil

Experiments have been conducted on the movement of gases and vapours in soil. The initial work was performed using gases such as methane for ease and comparative safety during the equipment and methods development stage.

Gas was introduced at the top or bottom of vertical, cylindrical soil columns, 8 cm dia. and 42 cm long. Samples were extracted in syringes and analyzed in a gas chromatograph with respect to time. The data exhibited diffusional behavior as anticipated and were used to test the Allan Model for gas migration.

Subsequent experiments are in progress using hexane and acetone in the column foot space as a liquid source to emit vapours for migration through the column. Data on vapour concentrations and emission rates have been collected. Limited model simulations have been done.

Construction of a large vapour flux chamber plus fume hood has been completed and will be used for large scale experiments on vapour movement in soil. Preliminary experiments have been completed.

EXPERIMENTS ON IMMISCIBLE LIQUID TRANSPORT IN SOIL

Immiscible fluids are of environmental concern today because:

- the variety and quantity of immiscible liquids have steadily increased,
- many of the immiscible liquids are toxic and/or carcinogenic,
- although only slightly soluble, immiscible liquids are often soluble at concentrations which are above levels considered safe, and
- immiscible liquids in soil being poorly soluble remain as a source of contamination for many years.

It is important to understand how immiscible liquids migrate through the ground because of the potential danger they pose to groundwater.

The theory of immiscible displacement was developed and put into practical use in the petroleum industry some time ago to assess the behavior of oil and gas in reservoirs and to optimize the effects of steam and water-flooding. However, the application of immiscible displacement theory to groundwater contamination scenarios is a relatively new practice. It is only in recent years that research in this area has taken place. The three major areas of research over this time are worthy of note.

One area of research has involved the movement of hydrocarbons from the surface of the ground to the top of the water table. Hydrocarbons are lighter than water and therefore do not migrate past the water table. Analytical expressions were developed to describe the movement of hydrocarbons in simplified situations and to find the distribution of water, air, and the hydrocarbon in the ground. Laboratory experiments were performed in sandboxes and columns to watch the movement of the hydrocarbon front and to get estimates of residual saturations. Papers in this area include work by Van Dam (1967), Schwille (1967), Mull (1971), Schiegg (1977), Dracos (1978), and Eckberg and Sunada (1984).

Another area of research has examined the migration of hazardous compounds that are heavier than water, most notably the low molecular weight solvents. These immiscible liquids being heavier than water generally sink past the groundwater table. They continue to move down until all the fluid is at residual saturation, or until an impermeable layer is reached, or until a layer with an entry pressure greater than the pressure that can be built up by the infiltrating fluid is reached. This research has looked at the migration of compounds in sandboxes and sand columns in different situations. Migration in the saturated and unsaturated zones were examined and the residual saturation of various compounds were investigated. This work was carried out mainly by Schwille ((1967), (1975), (1984)).

The newest area of research is the quantitative evaluation of contamination of groundwater by immiscible liquids. This involves the development of complex finite element or finite difference computer models to predict the movement of immiscible liquids in the ground. The most recent models in the literature include those of A.D. Little (1983), Faust (1985), Abriola and Pinder (1985), and Osborne and Sykes (1986). Verification of these models is done by comparing their results to the results of another model or to the 1-D analytical solution of Buckley and Leverett (1942).

The purpose of this research has been to further this understanding of the migration of immiscible fluids in soil and to furnish experimental data which can be used to verify simulation models.

1. Detection Methods

No standard method exists to measure the saturation of two immiscible liquids in a porous media as a function of time and location. However, a device is being developed as part of this work to make such measurements. The device, a thermal conductivity (TC) probe, consists of a "thermo" part or coil which pulses a certain amount of heat for a specified period of time and a "probe" part or senser which measures temperature. Depending on the thermal conductivity of the material(s) between the coil and the senser, a certain change in the temperature is experienced at the senser each time a pulse occurs. Since most immiscible liquids of a hazardous nature have a thermal conductivity approximately one-quarter that of water, it was felt that this device could be made to detect changes in the amount of water and immiscible liquid surrounding the probe.

The first step in development of the TC probe was to optimize the configuration of the probe so as to obtain the maximum measured temperature change between water and an immiscible liquid for a given pulse of heat. Several designs were tested and compared by taking temperature measurements in oil and water and looking at the difference in the measurements (ΔT) for each probe.

Based on maximum ΔT, the configuration shown schematically in Figure 1 was considered the best.

The second step in developing the TC probe was to examine the relationship between ΔT and spatial mixture of the immiscible fluids surrounding the probe. It was felt that a linear relationship would exist between ΔT and the % mixture of the immiscible fluids surrounding the probe.

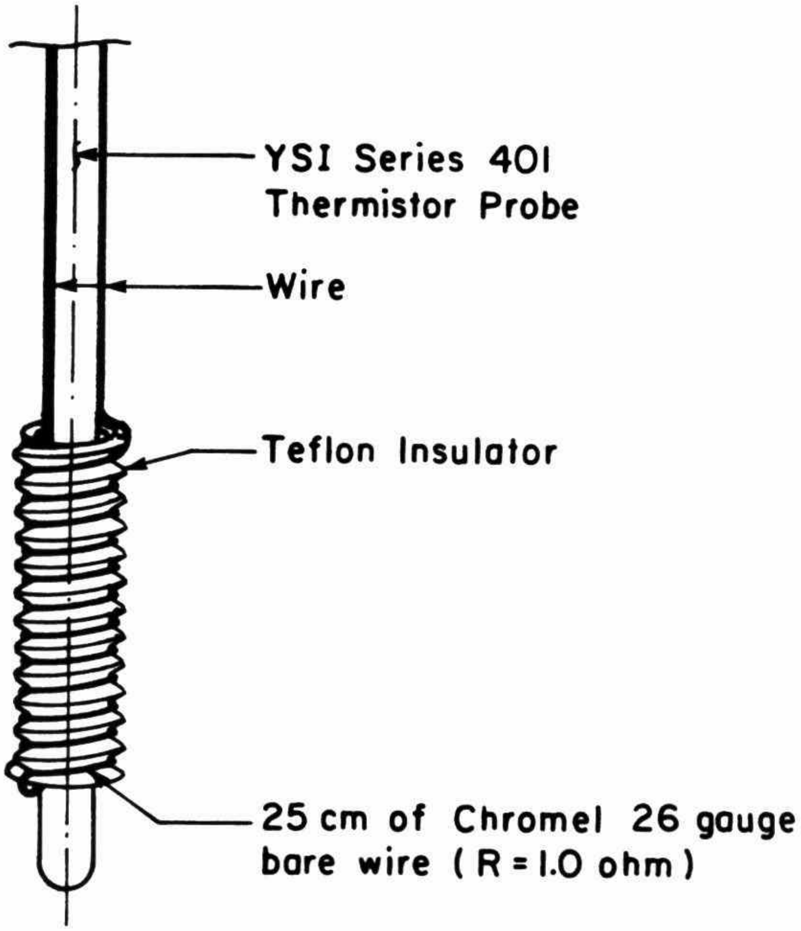
Attempts were made to make homogenous mixtures of different concentrations of oil and water. The change in temperature could then be measured by the probe for each mixture and a plot of the temperature change per heat pulse versus % oil (or water) made. Attempts to make homogeneous mixtures of oil and water were made by using conventional blenders, homogenizers, and by mixing by hand in a porous media. However, in each case the oil would start to separate from the water once mixing was stopped. Emulsifiers were then employed to keep the oil and water from separating. Both "Span-80" and "Triton" were used for this purpose with reasonable success as shown in Figure 2. While some scatter in the data are evident, there is clearly a linear relationship between ΔT and percent saturation (% H_2O in mixture). It is also shown that the presence of the emulsifier did not have a major effect on the ΔT response.

The third step in developing the TC probe was to look at factors that might change the reading of the probe other than just the spatial mixture of the immiscible fluids. The factors which were considered were the initial temperature of the fluids, the velocity of the fluids, and the previous wetting history of the soil. The effect of initial temperature of fluid on ΔT was found not to be significant. This was done by taking readings from the probe in water baths at temperatures from 18° C to 40° C. The ΔT readings showed no significant change over this temperature range.

The consequence of different fluid velocities would have on a reading was looked at by placing the probe in a column of saturated porous media. Water was passed through the column at various velocities and the probe readings recorded. The results indicate that, at higher velocities in the range of 3.0 cm.min^{-1} or greater, there is a significant effect on ΔT. However, a preliminary correction factor for this error has been established. For the range of velocities that have been expected with oil flow in soil (up to 0.4 cm.min^{-1}) the effect of velocity on ΔT can be neglected.

The experimentation done to assess the impact of previous wetting history on ΔT was done by placing the probe first in water, then in oil and then back into water. The readings recorded when the probe was in the water for the second time were initially different from the readings

THERMAL CONDUCTIVITY (TC) PROBE



Scale : Two times actual size

Figure 1

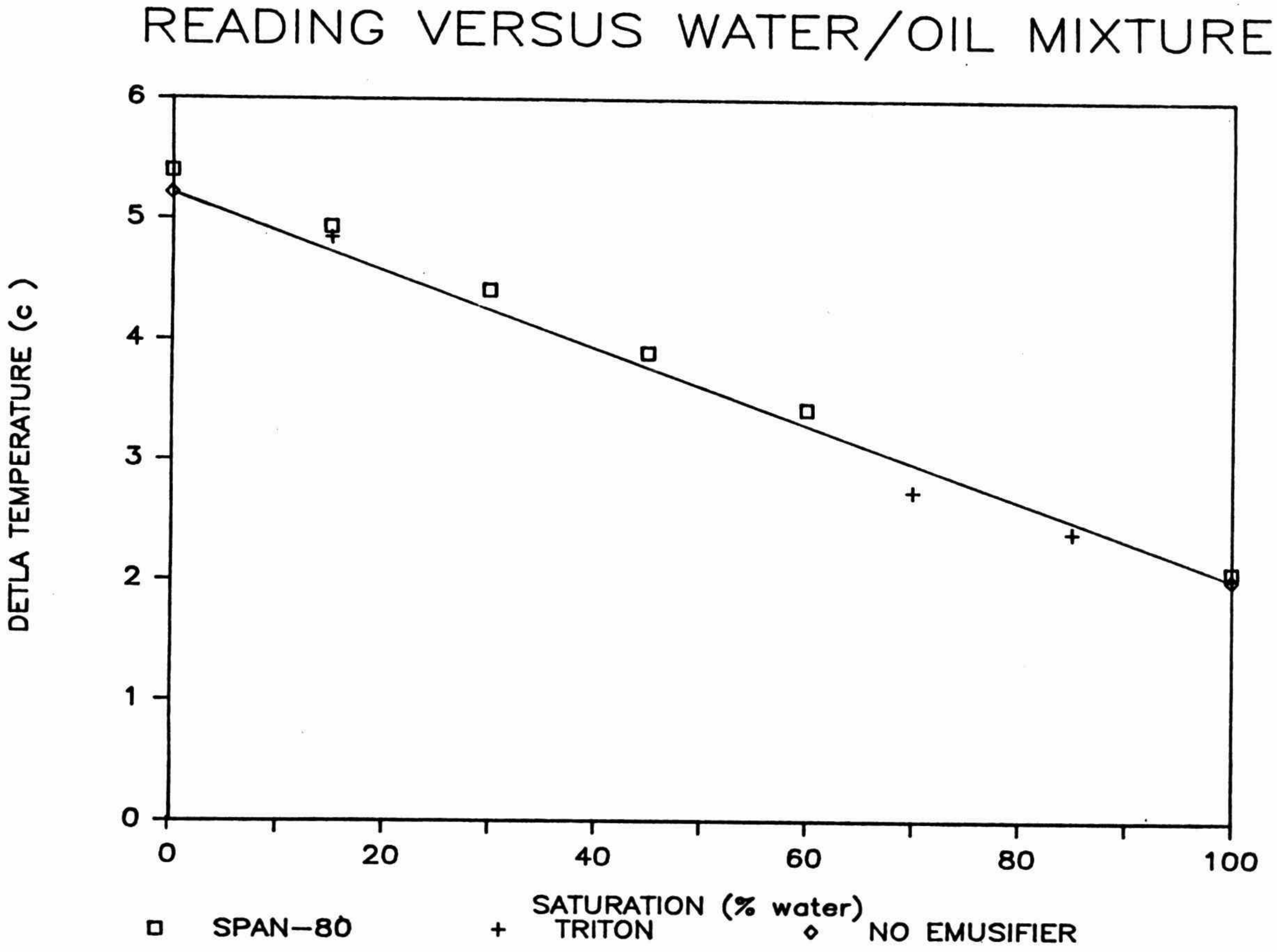

READING VERSUS WATER/OIL MIXTURE
DETLA TEMPERATURE (c)
0
1
2
3
4
5
6
0
20
40
60
80
100
SATURATION (% water)
□ SPAN-80
+ TRITON
◇ NO EMUSIFIER

Figure 2

recorded from when the probe was first in the water. However, the second readings gradually approached the first during which time, a visible film of oil appeared on top of the water. Thus, the wetting history did not appear to have a significant effect on ΔT if sufficient time were available between measurements. As well, in a porous media it is unlikely that such rapid changes in the spatial mixture of immiscible liquids as used in this experiment would occur.

2. Column Experiments On Immiscible Liquid Transport

Several experiments have been performed to examine the movement of immiscible liquids in soil to provide a basic understanding of the processes involved, to test the TC probe and to quantify the transport as a data base for model evaluation. The equipment used was described previously. The liquid used was coloured oil for the initial development work. However, other hazardous liquids are now being studied. All experiments involved upflow imbibition of oil into water saturated sand at constant heads (6 cm H_2O). Two TC probes were located in the 54 cm depth of sand at 21 cm and 40 cm up from the bottom.

The results of two experiments are shown in Figures 3, 4 and 5. Figures 2 and 4 show the experimental data recorded as ΔT, the lower and upper TC probe output versus time measured from the time of oil entry to the column. Since the thermal conductivity of the oil is less than H 0, ΔT for oil is greater. Relative saturations range from 100 H_2O (0% oil; $\Delta T \simeq 1.25°$ C) to 0% H_2O (100% oil; $\Delta T \simeq 1.85°C$). The results show that the oil front was only slightly dispersed with passage from 0 to 100% oil occurring in approximately 20 minutes at the lower probe. The oil used in Experiment 3 was more viscous than for Experiment 2, producing a lower permeability and a slower velocity as shown in a comparison between Figures 3 and 4. The data appear to be very good with only limited scatter.

Figure 5 compares the results from Experiments 2 and 3 by normalizing the data from ΔT values to % oil saturation and by adjusting the time axis from Experiment 3 to that of Experiment 2 because of viscosity differences due to different experimental temperatures. This comparison at the lower probe is excellent with a 10 minute differential shown at the upper probe. The favourable comparisons between the two experiments are a measure of TC probe reliability.

The information shown in Figure 6 is in the form of fluid velocity with respect to time for Experiments 2 and 3. As the theory related to the Darcy Equation states, the velocity of the fluid mixture within the column will reduce as the % oil in the column increases. Oil travels more slowly than water and, because of the upflow configuration, the oil regulates the flow. As the height of the oil increases, the hydraulic gradient also reduces. Thus, the first order decay in velocity as shown in Figure 6 is reasonable. Normalized comparisons between Experiments 2 and 3 are excellent.

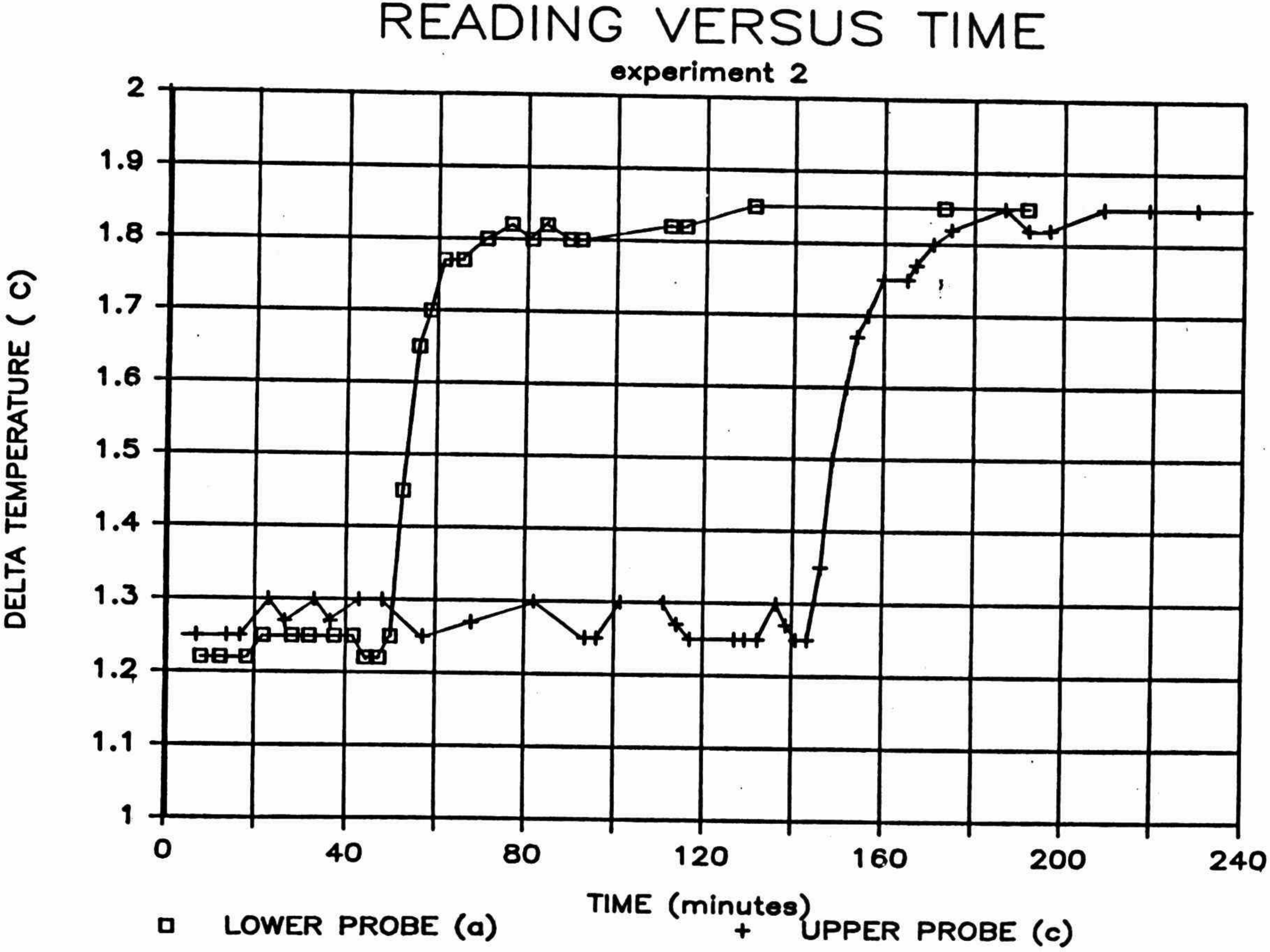

READING VERSUS TIME
experiment 2
DELTA TEMPERATURE (C)
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0
40
80
120
160
200
240
TIME (minutes)
LOWER PROBE (a)
UPPER PROBE (c)

Figure 3

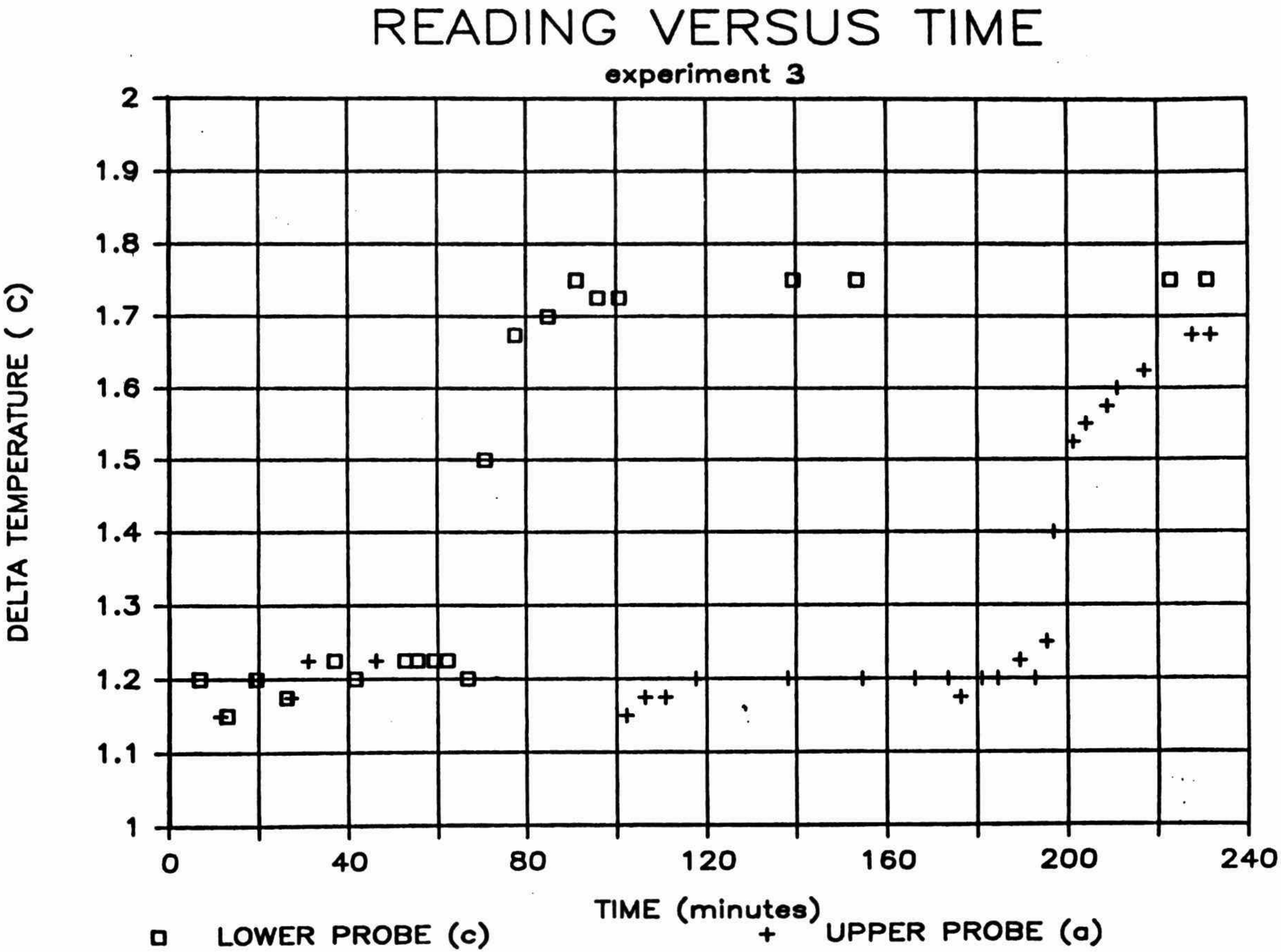

READING VERSUS TIME
experiment 3
DELTA TEMPERATURE (C)
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0
40
80
120
160
200
240
TIME (minutes)
□ LOWER PROBE (c)
+ UPPER PROBE (a)

Figure 4

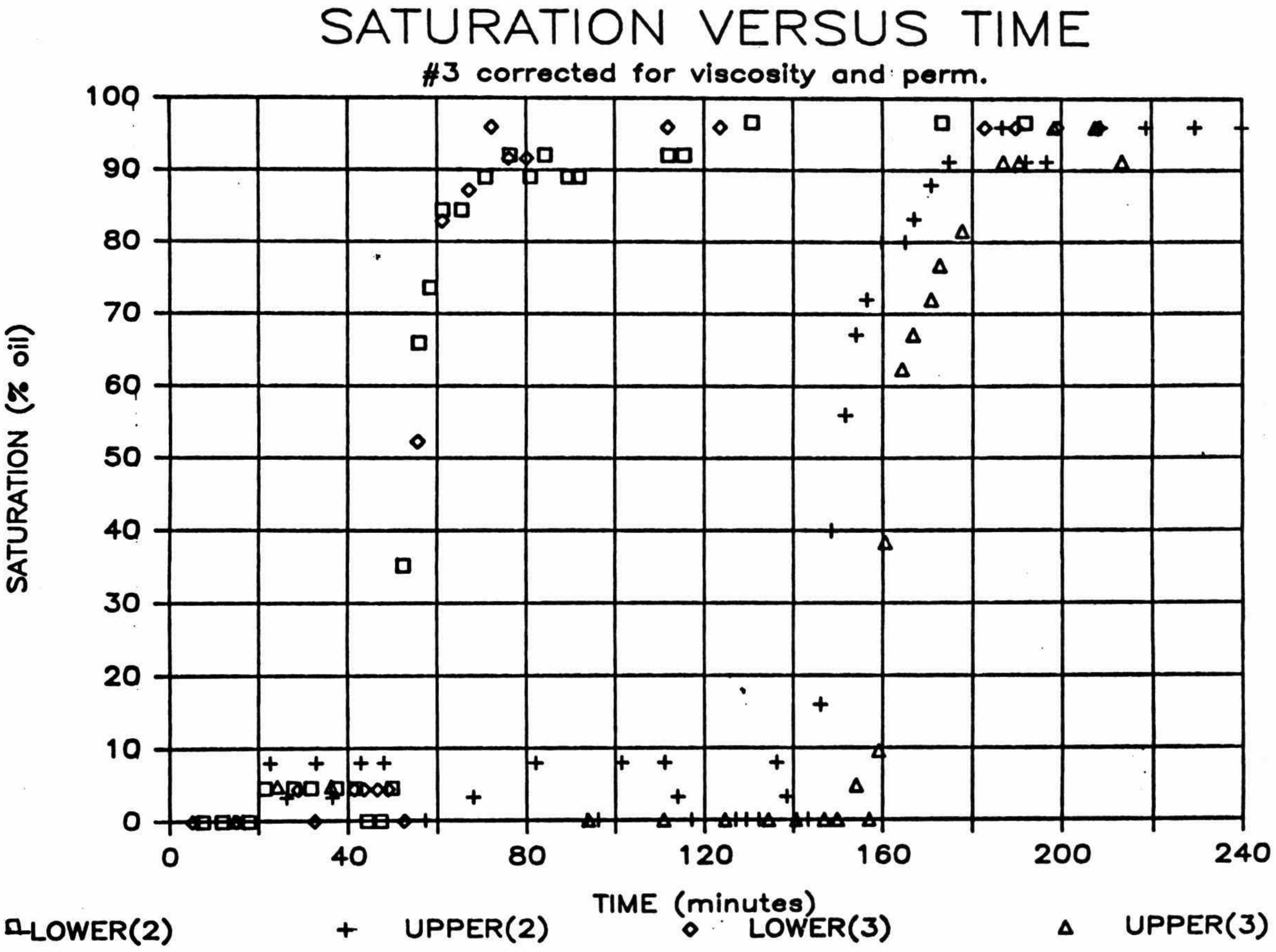

SATURATION VERSUS TIME
#3 corrected for viscosity and perm.
SATURATION (% oil)
100
90
80
70
60
50
40
30
20
10
0
0
40
80
120
160
200
240
TIME (minutes)
LOWER(2)
UPPER(2)
LOWER(3)
UPPER(3)

Figure 5

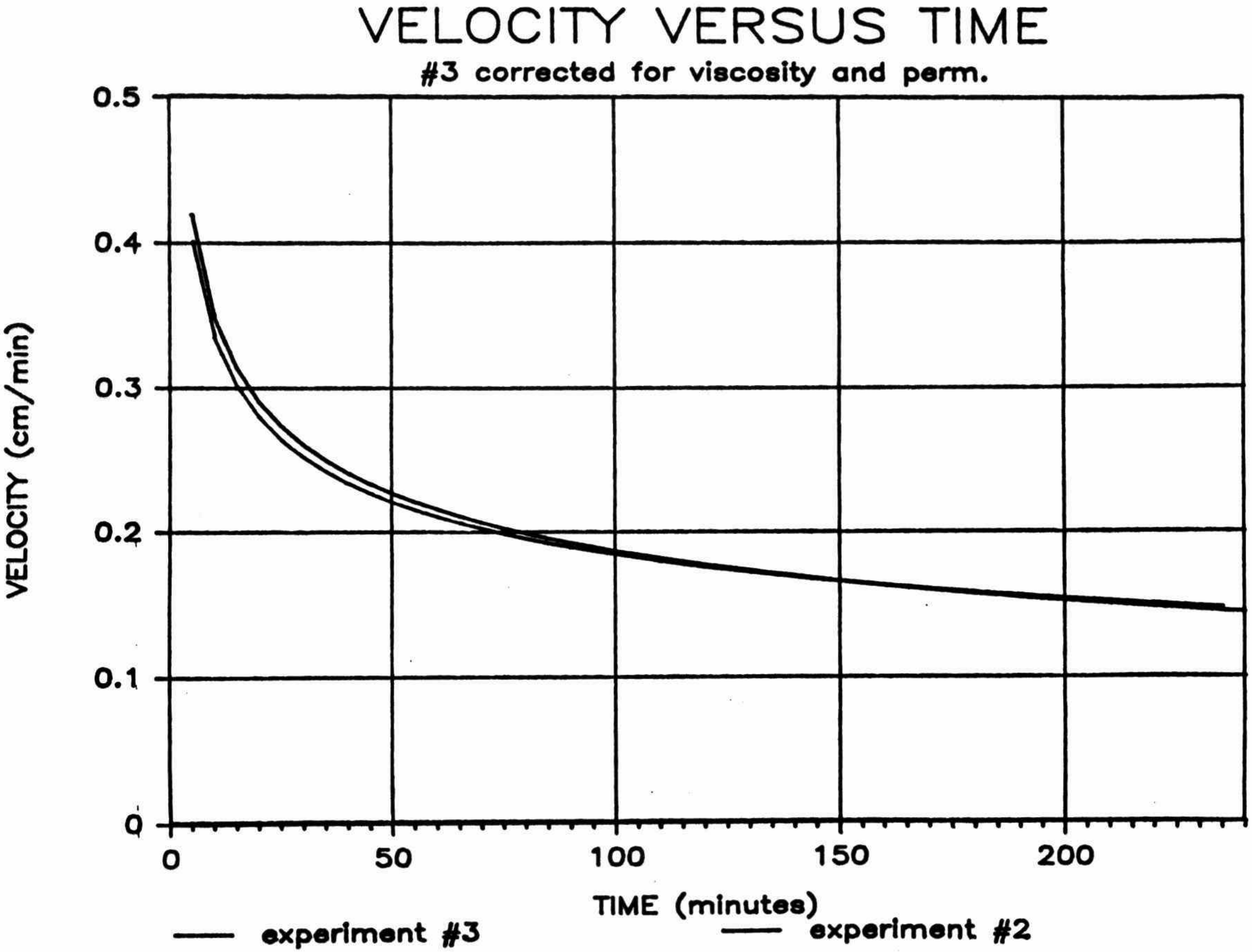

VELOCITY VERSUS TIME
#3 corrected for viscosity and perm.
0.5
0.4
0.3
0.2
0.1
0
VELOCITY (cm/min)
0
50
100
150
200
TIME (minutes)
experiment #3
experiment #2

Figure 6

3. Measurements of Relative Permeability and Capillary Pressure vs. Relative Saturation

Relationships between relative permeability and capillary pressure versus relative saturation are essential to quantifying movement of multiphase fluid systems in soil. As identified previously, limited experimentation of this nature has been done for oil-water mixtures but very little for other immiscible liquids. Consequently, this experimental series was designed to fill this need by developing improved experimental methods and then applying them to liquids other than oil.

The experimental method involved use of the standard column of this research to which varying proportions of oil and H_2O were added at constant flow rates. Steady state was defined as the point at which the oil-H_2O proportions of the effluent became steady. The combined discharge velocities and the applied pressure heads were used to calculate the relative permeabilities. The results of the first experiment performed are shown in Figure 7. This is for the drainage curve and since the relative permeability curves are hysteretic, the imbibition curve will also have to be developed.

Although the results are preliminary, they have the proper form and thus confirm the utility of the method chosen. It must be noted that these experiments are non-destructive because of the use of the TC probe. All prior experiments have required that, for each pair of points on the curve, the column be taken apart and the relative saturation be determined using a separate experiment. The continuous flow, non-destructive method developed here is thus a great improvement in methodology. It will be subsequently applied to other immiscible liquids in this work.

The results of preliminary experiments to quantify capillary pressure versus % water saturation for drainage conditions are shown in Figure 8. In this case water is the wetting fluid and oil is the non-wetting fluid.

EXPERIMENTS ON VAPOUR MOVEMENT IN SOIL

The movement of hazardous vapours in soils is being examined on two different scales. Soil columns 7 cm in diameter and 36 cm high have been utilized to study the movement of methane, hexane and acetone vapours through fine sand. A large rectangular chamber referred to as a flux box has also been constructed, together with the necessary safety exhaust system. The box has been constructed so that either gases, such as methane, or liquids, such as hexane, heptane or acetone, may be exposed to the soil. Preliminary studies with the flux box are being carried out with methane. Once experimental procedures have been refined, tests will be carried out with one or more of the volatile HIL's.

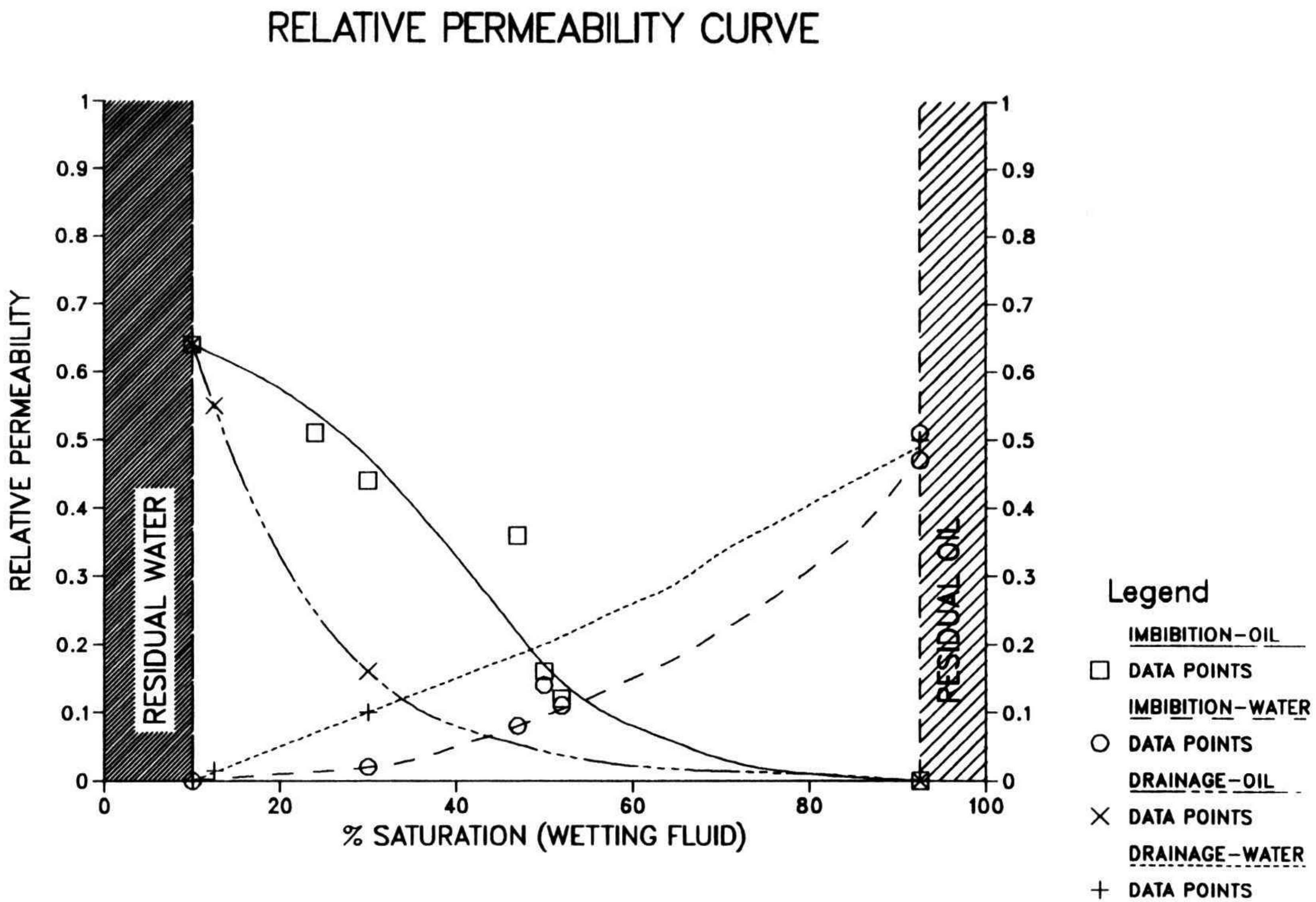

RELATIVE PERMEABILITY CURVE
RELATIVE PERMEABILITY
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
RESIDUAL WATER
RESIDUAL OIL
0
20
40
60
80
100
% SATURATION (WETTING FLUID)
Legend
IMBIBITION-OIL
DATA POINTS
IMBIBITION-WATER
DATA POINTS
DRAINAGE-OIL
DATA POINTS
DRAINAGE-WATER
DATA POINTS

Figure 7

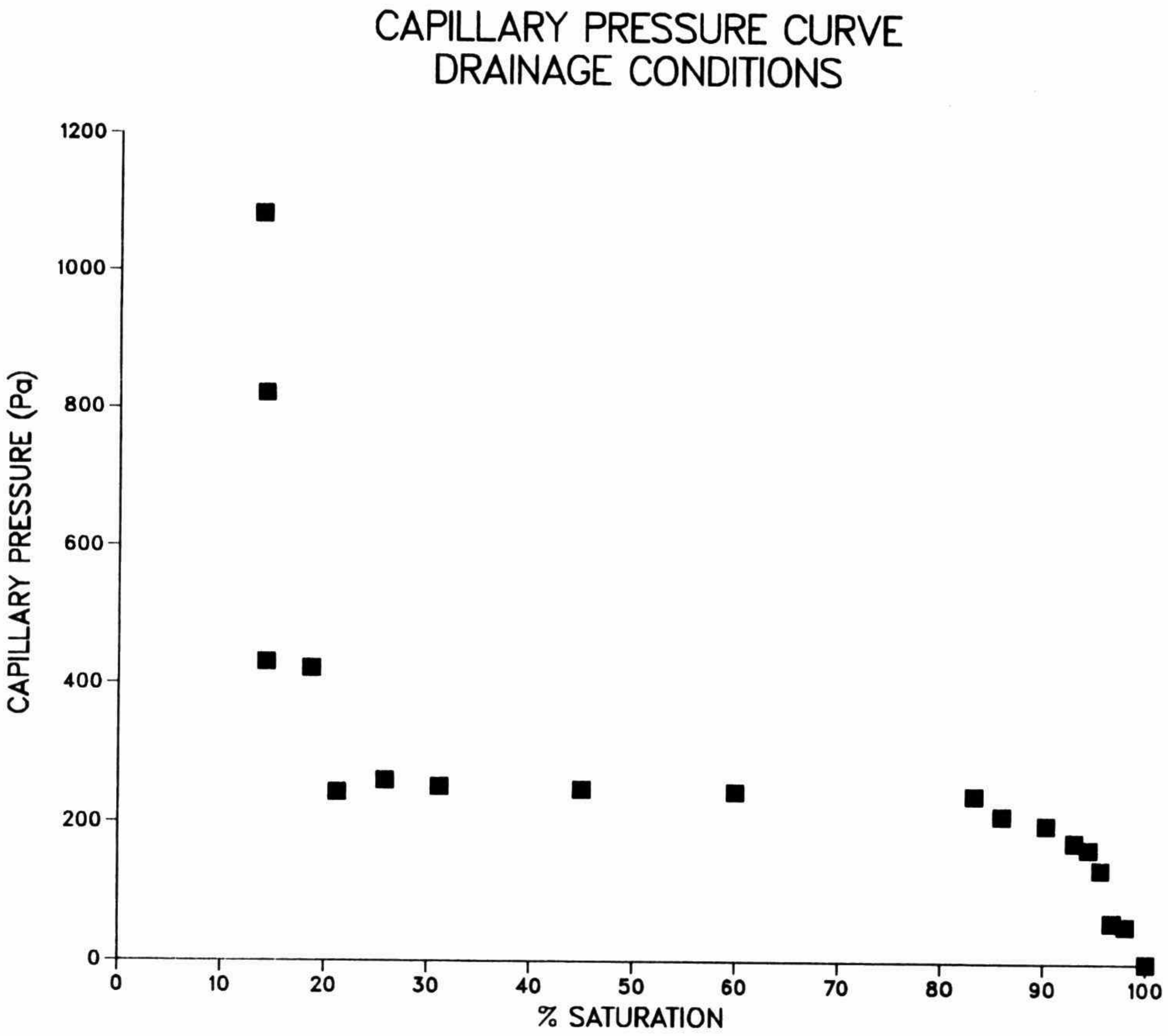

CAPILLARY PRESSURE CURVE
DRAINAGE CONDITIONS
CAPILLARY PRESSURE (Pa)
1200
1000
800
600
400
200
0
0
10
20
30
40
50
60
70
80
90
100
% SATURATION

Figure 8

1. Soil Column Experiments

Plexiglass cylinders containing a fine Ottawa sand serve as the test columns identified above. The ends of the column are closed except for two ports for the introduction of vapour and for pressure control. An open volume approximately 5 cm high is maintained at the top (head space) and the bottom (foot space) of the column. A gas contaminant can be introduced into either end of the column, depending upon experimental protocol. A small airflow is introduced at the opposite end to insure that no contaiminant build-up occurs thus maintaining a zero concentration condition at the discharge boundary end. The pressure ports maintain atmospheric pressure in the head and foot spaces. Therefore, the only vapour migration into and through the soil is due to diffusion and for body forces.

Sampling ports are located at 7.5, 15.0, 22.5 and 30.0 cm from the contaminant source. Sampling methods to date have utilized syringes and hypodermic needles to draw small quantities of the soil gas mixture for analysis in a gas chromatograph. Standard laboratory septums are used to seal the sampling ports. Gas concentrations in the head and foot spaces are sampled through the pressure port.

Column Experiments With Methane

A number of experiments on the diffusion of methane through porous media have been carried out with the soil columns. Figure 9 presents the results of two parallel experiments expressed as methane concentrations with time at the four sampling ports in the column. The gas was introduced into the head space, where the concentration stabilized at 87.6 percent for the length of the experiment. It can be seen that the gas concentration rate of change and the eventual stable concentration level is inversely proportional to the port distance from the source. In fact, 75 minutes into the experiment, the column concentrations have stabilized at what appears to be a linear concentration gradient from the head space (at 86% methane) to the foot space (at 0% methane).

The results from the first experiment are represented by the dotted lines while the symbols are from the second, parallel experiment. The replication is excellent. Figure 10 shows a comparison between the methane column experiments and simulations created through the use of the Allan Model developed earlier by this project. The comparison is excellent.

Column Experiments With Hexane

Experiments with volatile organic liquids as the vapour source required some basic modifications to the column. For hexane, the foot space was sealed off after 25 ml of liquid was in place in a foil pan. A temperature probe was inserted in the foot space to monitor the temperature range just above the liquid. The volatilization rate of hexane is temperature dependent. Therefore, the temperature readings were monitored for comparison to the measured vapour concentration with time in the foot space. A manometer was used to monitor the foot space for any pressure variation. A standard air purge, like that used in the

Figure 9: CH4 MIGRATION – EXPERIMENT 3 REPLICATION

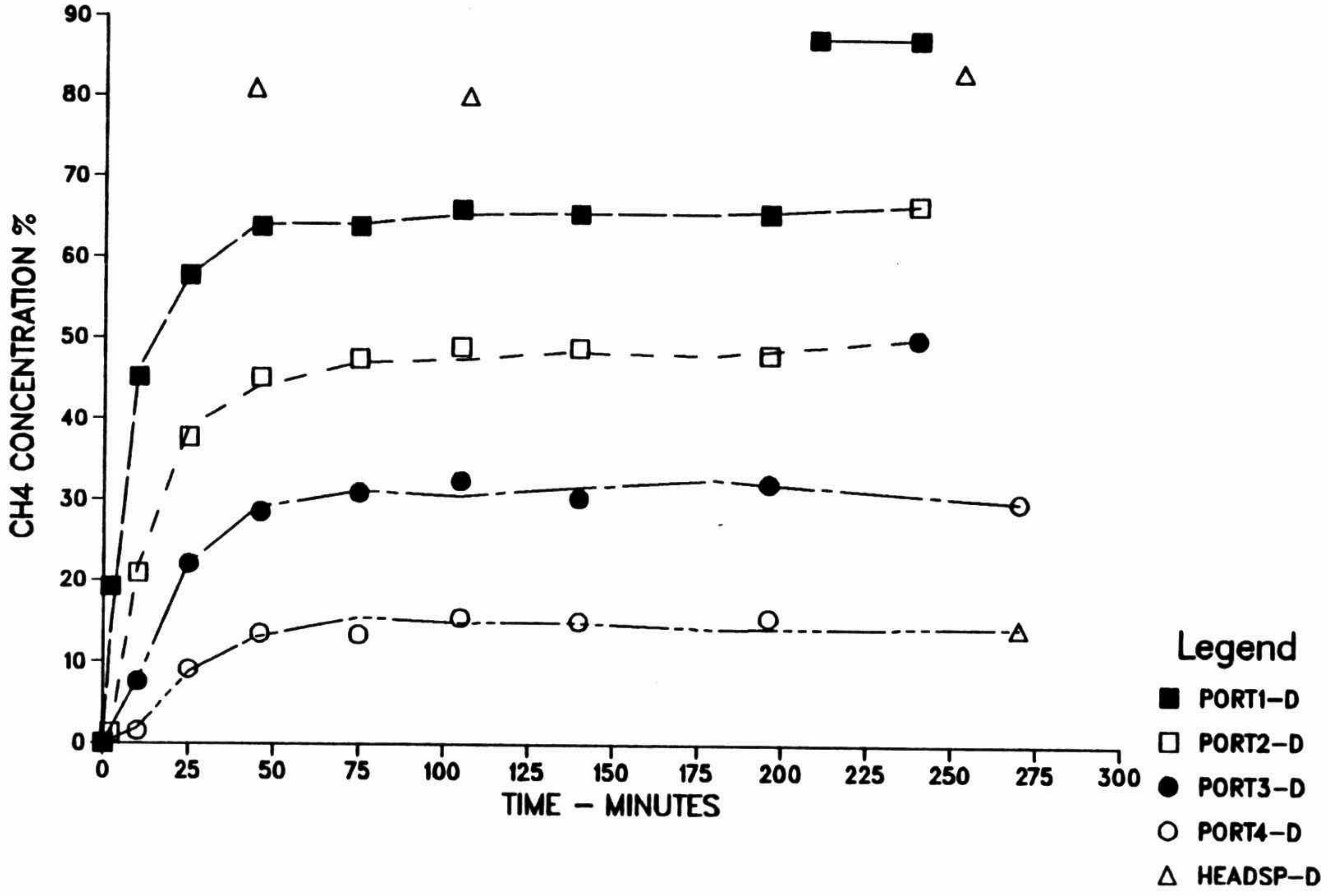
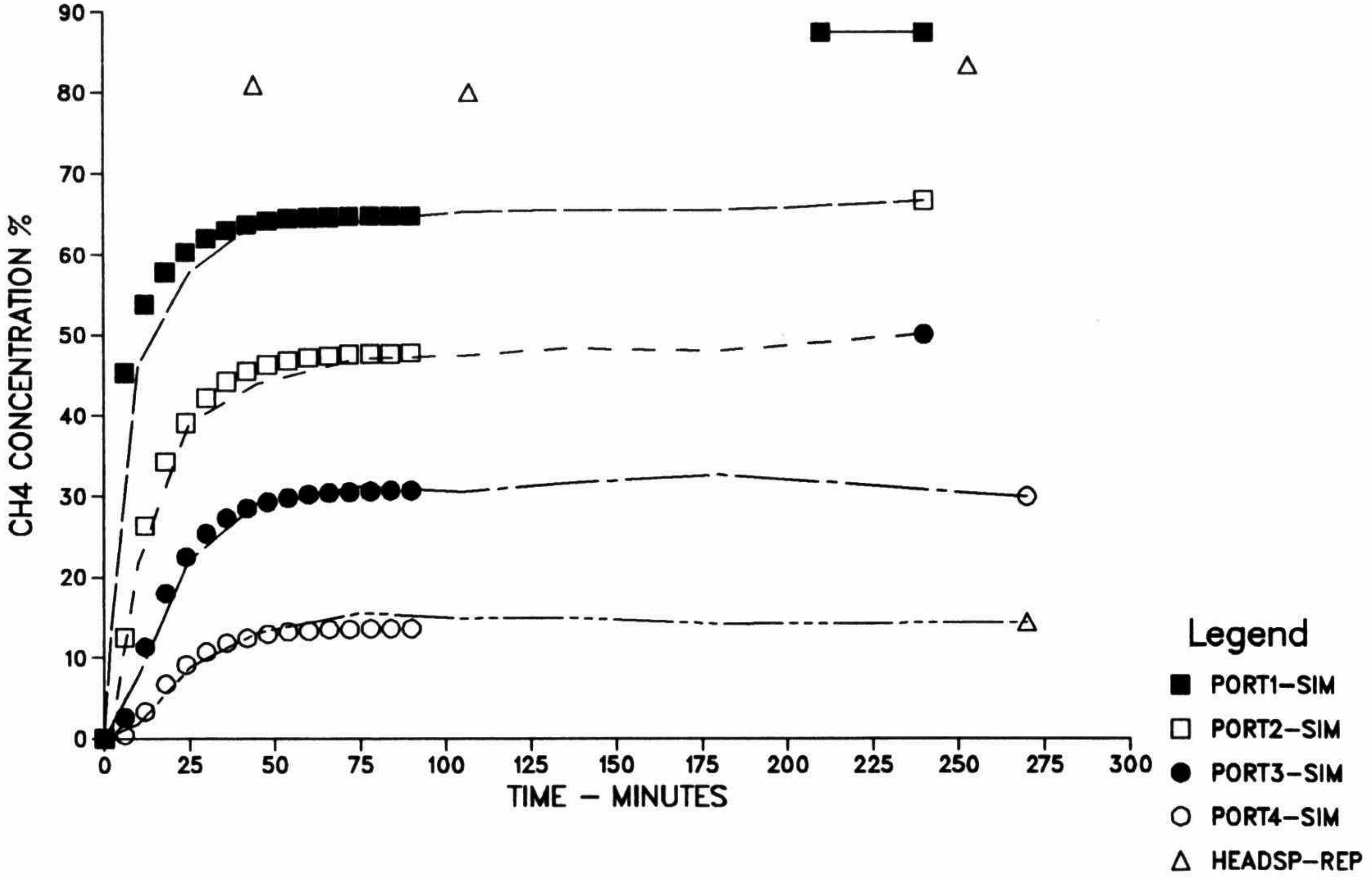


Figure 10: CH4 MIGRATION – EXPERIMENT 3 SIMULATION



82% HEADSPACE

methane column experiments, was applied to the head space to maintain an approximate zero concentration.

The results of a hexane column experiment are presented in Figure 11. The concentrations in the foot space and the sampling port nearest the source demonstrate somewhat erratic behaviour. However, this behaviour appears to be related to minor temperature fluctuations in the laboratory, resulting in significant variation in the vapour pressure of the liquid hexane.

The vapour concentrations appear to be less sensitive to head space concentration variation with distance. At ports 3 and 4, 23 and 30 cm from the source respectively, the hexane vapour concentrations showed reduced variation. The conclusion that can be drawn from this is that concentration variations recorded at the column source may be neglected for the large scale experiments such as the sandbox and in numerical modelling of vapour migration from a HIL's spill site.

A problem with condensation of hexane vapour within the sand column was anticipated and has been observed.

Column Experiments With Acetone

The results of a column experiment with acetone are presented in Figure 12. The "y" axis data are presented as a percent of the mean head space concentration (100%). For this reason, small anomalies such as head space concentration of greater than 100% were possible.

2. Flux Box Experimentation

The flux box (3.6 m long x 1.2 m high x 0.3 m wide) was designed for larger scale vapour transport experiments in soil. Source liquids can be introduced along the base of the box or within the soil at various points. Ports for sample extraction by syringe and pressure measurement exist along the sides of the box. The soil surface can be open or sealed, vegetated or stripped and quiescent or exposed to wind to study transport at this important discharge boundary.

Preliminary experiments have been conducted with methane as the source gas at the centreline of the base and Ottawa sand as the medium. Methane concentrations in the soil as % by volume after 68 and 92 minutes are shown in Figures 13 and 14 for one-half of the symmetrical box. No pressure gradient existed across the box from the source to the upper open discharge surface. The methane contours are consistent with transport by diffusion.

FIGURE 11: HEXANE MIGRATION IN COLUMN EXPERIMENT 2

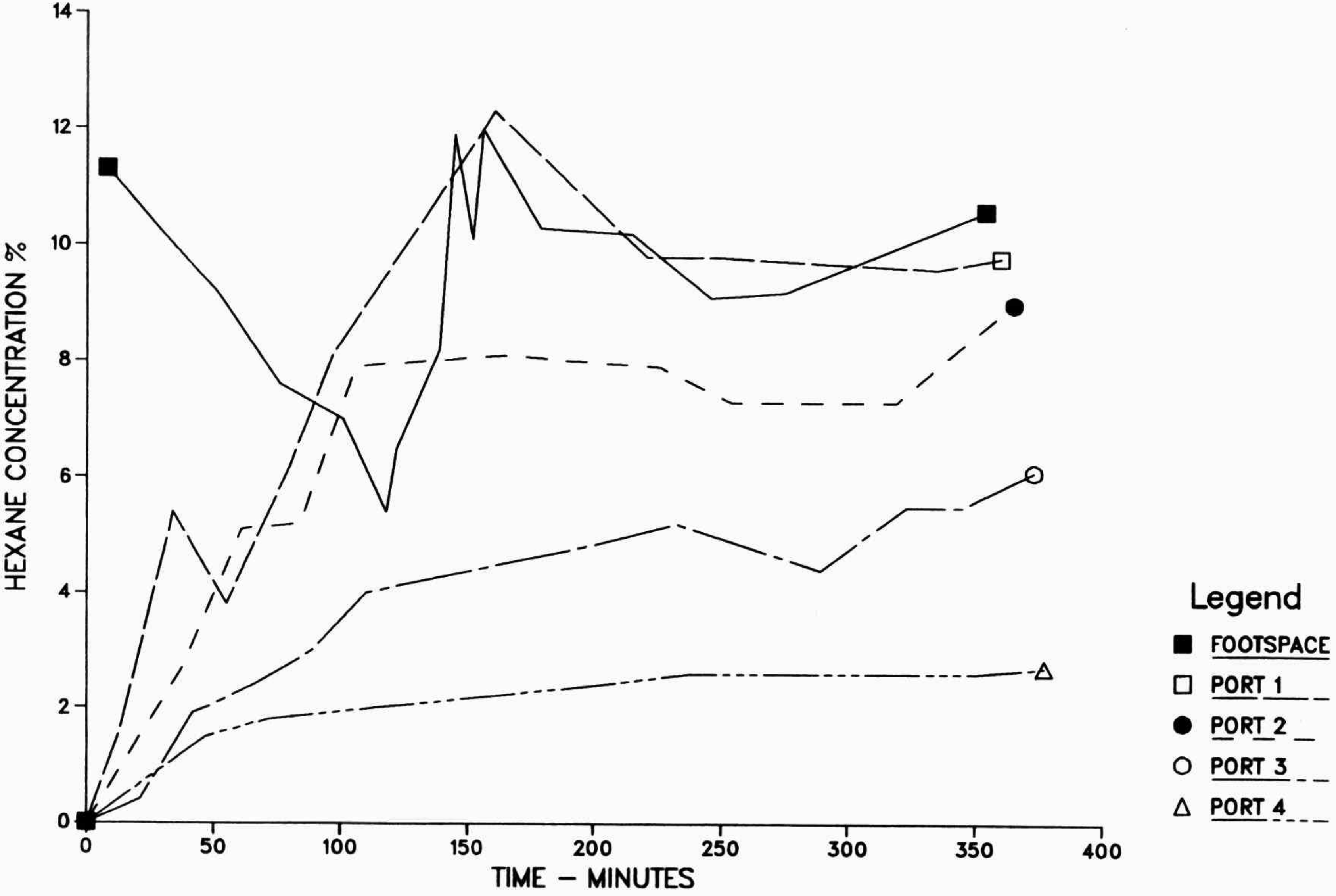
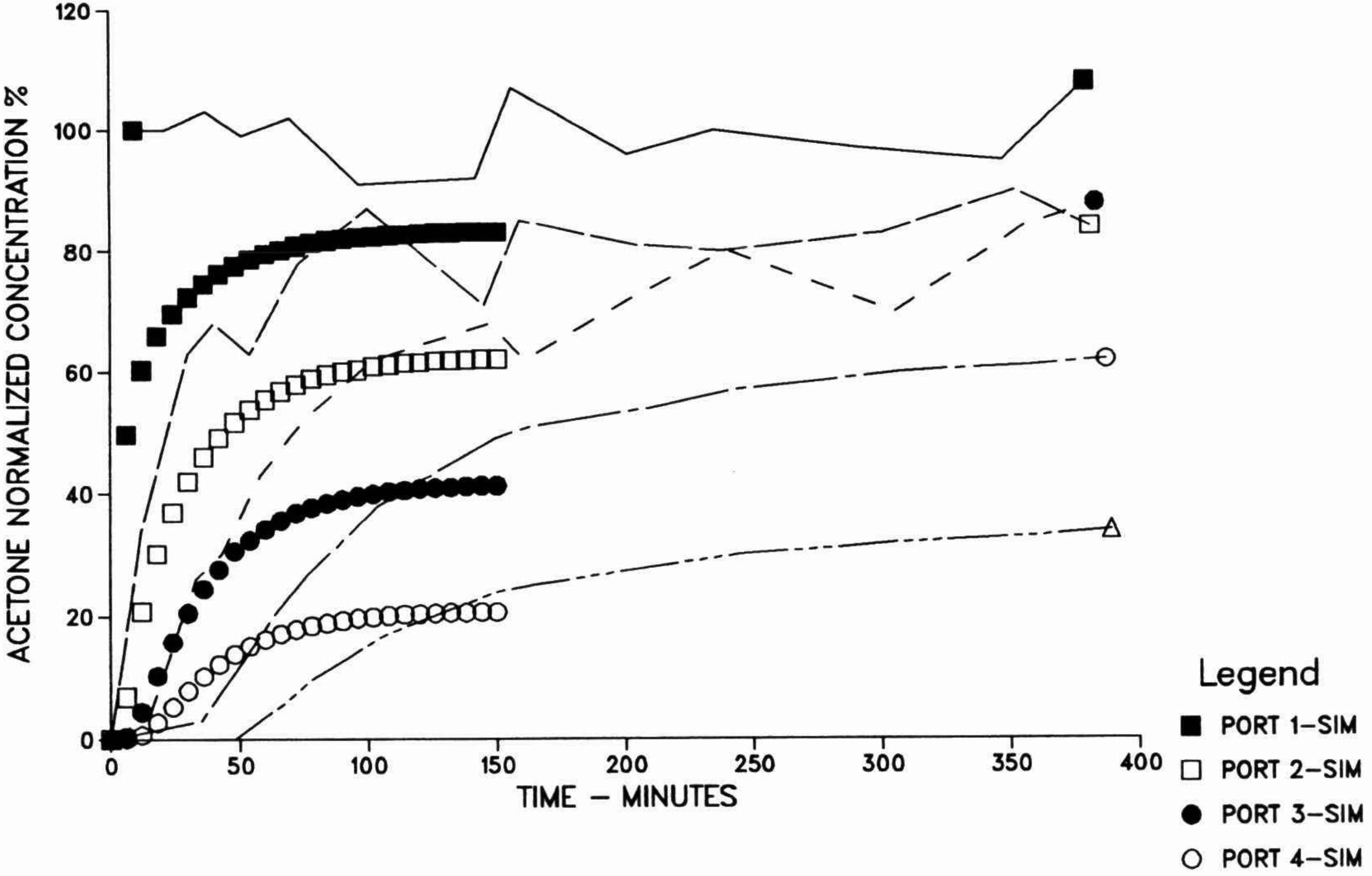


Figure 12: SIMULATION OF ACETONE COLUMN EXPERIMENT



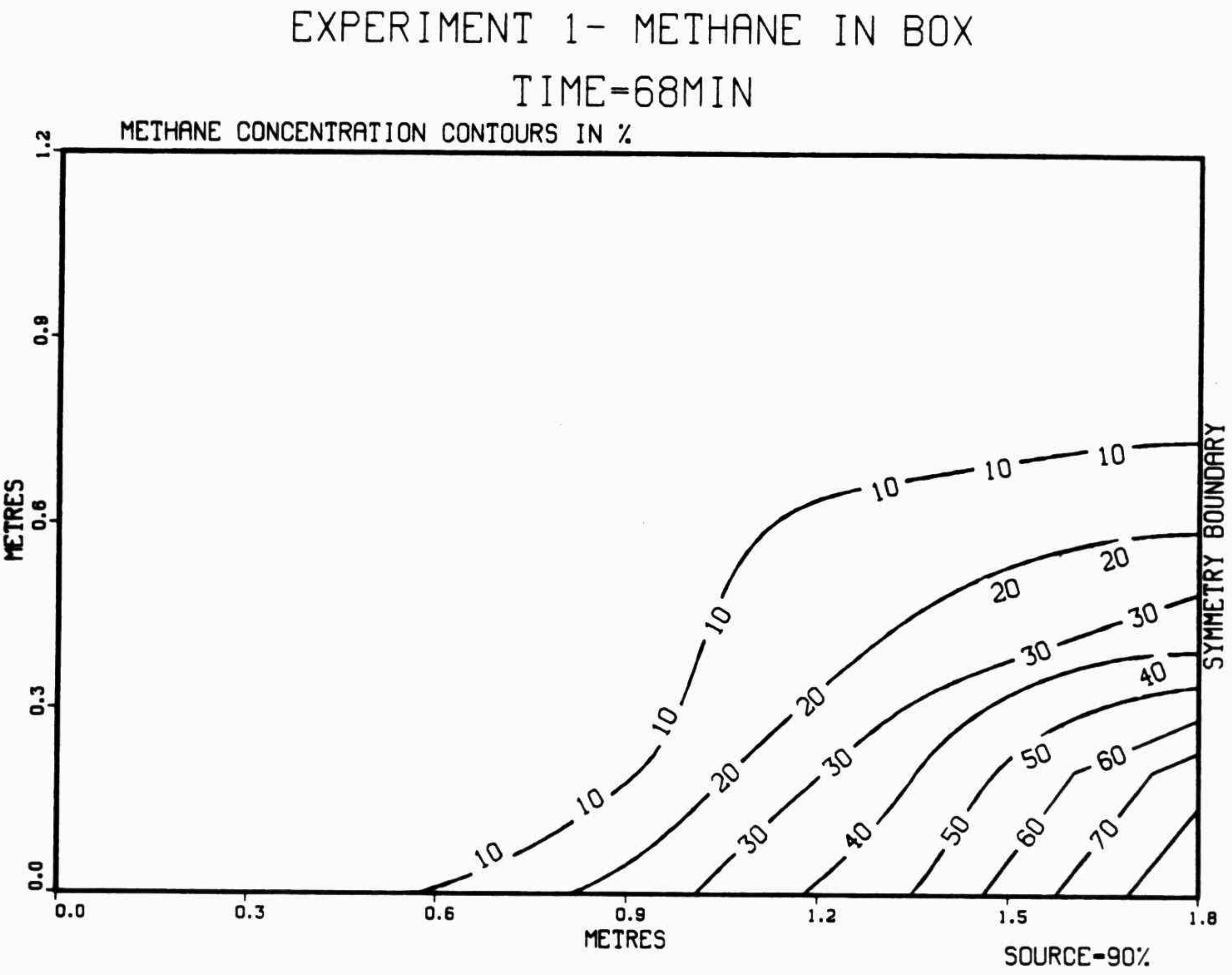

EXPERIMENT 1- METHANE IN BOX
TIME=68MIN
METHANE CONCENTRATION CONTOURS IN %
METRES
0.0
0.3
0.6
0.9
1.2
METRES
0.0
0.3
0.6
0.9
1.2
1.5
1.8
SYMMETRY BOUNDARY
10
20
30
40
50
60
70
SOURCE=90%

Figure 13

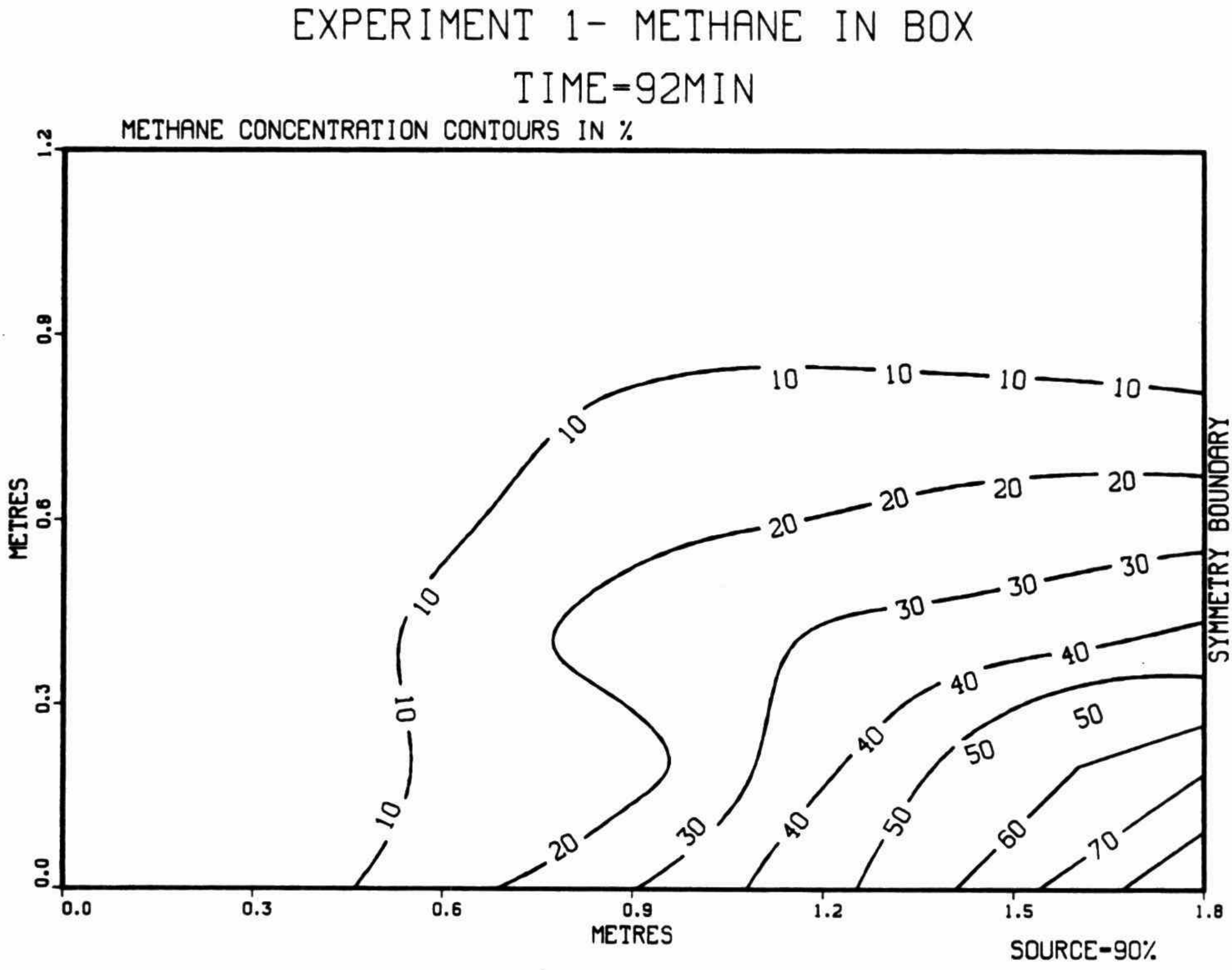

EXPERIMENT 1- METHANE IN BOX
TIME=92MIN
METHANE CONCENTRATION CONTOURS IN %
METRES
0.0
0.3
0.6
0.9
1.2
METRES
0.0
0.3
0.6
0.9
1.2
1.5
1.8
SYMMETRY BOUNDARY
SOURCE=90%
10
20
30
40
50
60
70

Figure 14

REFERENCES

Abriola, L.M., and Pinder, G.F., 1985. "A Multiphase Approach to the Modeling of Porous Media Contamination by Organic Compounds 2. Numerical Simulation". Water Resour. Res. 21, 19 (1985).

Allan, R.E., 1986. "Modelling and Sensitivity Analysis of Vapour Migration in Soil from Spilled Volatile Liquids". Masters Thesis, University of Waterloo, Waterloo, Ontario.

Bear, J., 1970. "Two-Liquid Flows in Porous Media", from Advances in Hydroscience, Vol. 6, Ven Te Chow, Ed., Academic Press, New York, pp. 141-152.

Buckley, S.E. and M.C. Leverett, 1942. "Mechanism of Fluid Displacement in Sands", A.I.M.E., 146.

Dracos, T., 1978. "Theoretical Considerations and Practical Implications on the Infiltration of Hydrocarbons in Aquifers", Proc. International Symp. on Ground Water Pollution by Oil Hydrocarbons, Prague (June 5-7).

Eckberg, D.K. and D.K. Sunada, 1984. "Non Steady Three-Phase Immiscible Fluid Distribution in Porous Media", Water Resour. Res., 20 (12).

Farquhar, G.J. and E.A. McBean, 1984. "Assessing the Behaviour of Hazardous Liquids Spilled Onto Soils", presented at Technology Transfer Conference No. 5, Ontario Ministry of the Environment, Toronto, Ontario.

Faust, C.R. 1985. "Transport of Immiscible Fluids Within and Below the Unsaturated Zone: A Numerical Model", Water Resour. Res. 21, 4.

Little, A.D., 1983. "5-Area Two Phase Flow Model", Ref. 84204-31, Arthur D. Little, Cambridge, Mass.

Osborne, J.M., 1984. "Numerical Modelling of Immiscible Two-Phase Flow in Porous Media". Masters Thesis, University of Waterloo, Waterloo, Ontario.

Osborne, M. and J. Sykes, 1986. "Numerical Modelling of Immiscible Organic Transport at the Hyde Park Landfill", Water Resour. Res., 22, 1.

Raisbeck, J.M. and M.F. Mohtadi, 1974. "The Environment Impact of Oil Spills on Land in the Arctic Regions". In Water, Air, and Soil Pollution, pp. 195-208, Reidel Publishing, Dordrecht, Holland.

Shiegg, H.O., 1977. "Methode zur Abschatzung der Ausreitung von Erdolderivaten in mit Wasser und Luft Erfullten Boden", Mitt. Versuchsanst. Wasserbau Eidgenis. Tech. Hochsch. Zurich, 22.

Schwille, F., 1984. "Migration of Organic Fluids Immiscible with Water in the Unsaturated Zone". In: Pollutants in Porous Media, The Unsaturated Zone Between Soil Surface and Groundwater, Ed: B. Yaron, G. Dagan, J. Goldsmith, Springer-Verlag, New York, pp. 27-48.

Schwille, F., 1975. "Groundwater Pollution by Mineral Oil Products". Proceedings of Moscow Symposium on Groundwater Pollution, August 1971, IAHS-AISH Publ. No. 103, pp. 226-240.

Schwille, F., 1967. "Petroleum Contamination of the Subsoil - A Hydrological Problem". IN: The Joint Problems of the Oil and Water Industries, Ed: Peter Hepple, The Institute of Petroleum, London, pp. 23-54.

Van Dam, J., 1967. "The Migration of Hydrocarbons in Water-Bearing Stratum". In: Joint Problems of the Oil and Water Industries, Ed: Peter Hepple, The Institute of Petroleum, London, pp. 55-96.

Wall, R.W., 1984. "Numerical Modelling of the Spill of Volatile Toxic Liquids Over Porous Media". Masters Thesis, University of Waterloo, Waterloo, Ontario.

DEVELOPMENT OF POLYSULFIDE TECHNOLOGY FOR TREATMENT OF CONCENTRATED SPENT CYANIDE LIQUORS

by

J.J. Ganczarczyk, Guichun Tang, and S.R. Bilevicius
Department of Civil Engineering
University of Toronto
Toronto, Ontario M5S 1A4

DEVELOPMENT OF POLYSULFIDE TECHNOLOGY FOR TREATMENT OF CONCENTRATED SPENT CYANIDE LIQUORS

INTRODUCTION

Concentrated spent cyanide liquors are by-products of several different industrial processes. Although they are usually produced in relatively small quantities, their storage, transport, treatment, and disposal present considerable hazards and serious technological difficulties. Examples of spent liquors are spent cyanide solutions from electroplating and metal finishing shops, and barren bleed solutions from gold and silver extraction operations.

Concentrated cyanide solutions often accumulate in electroplating and metal finishing shops. These accumulations of 4.5 to 9.0 m^3, which may be collected over a period of years, are generally 1 to 3% cyanide, although higher concentrations may occur.

Disposal of these concentrated cyanide-containing wastewaters poses considerable problems to the waste generator. Waste haulers are often reluctant to transport these wastes because of the difficulties and expense of final disposal. Transportation of these highly toxic wastewaters involves considerable risk, as leakage or rupture of the tanker would result in a potentially lethal situation. These disposal problems are of particular concern to operators of electroplating and metal finishing shops that are usually located in highly populated urban areas. Often, the concentrated cyanide-containing wastewaters remain stored in tanks and create a hazardous situation for workers. Sometimes these wastewaters are discharged in a clandestine fashion into the municipal sewer system, creating problems downstream.

Considerable efforts have been devoted to the treatment of cyanide-containing wastewaters and several treatment technologies have been developed.

A well-known and commonly used treatment method for cyanide-containing wastewaters, particularly in the electroplating industry, is the alkaline-chlorination oxidation process which is practically applicable for wastewater containing up to 500 mg/L CN^{-2}. Other treatment processes include: peroxide oxidation; iron precipitation; ozonation with ultraviolet irradiation; carbon adsorption with catalytic oxidation; formaldehyde treatment; electrolytic oxidation; and catalytic SO_2 treatment.

Some of the common technologies available for the treatment of cyanide-containing wastewaters are not applicable to concentrated cyanide liquors. Some treatment methods are associated with high capital and operating costs, or operational complexities than render them unsuitable for small industrial plants.

A relatively new technology available for treatment of cyanide-containing wastewaters is that of polysulfide application. Polysulfide-sulfur is commercially available in a number of forms i.e. calcium polysulfide (limesulfur) or sodium polysulfide (zinc purifier). These products usually contain between 15 and 30% polysulfide-sulfur. The reaction between cyanide and polysulfide-sulfur can be simply expressed by the equation:

$$CN^- + CaS_xS \rightarrow SCN^- + CaS_{x-1}S$$

Along with the conversion of cyanide to thiocyanate, polysulfide-sulfur reacts with the metal ions present to form metal sulfides:

$$M^{++} + CaS_xS \rightarrow MS + CaS_{x-1}S$$

The required dosage of polysulfide-sulfur to convert cyanide to thiocyanate must, therefore, be greater than stoichiometric requirements (i.e. CN: poly-S^o $>$ 1:1.23).

PREVIOUS WORK

The reaction of cyanide with polysulfide-sulfur to form thiocyanate was used as early as 1896 to remove hydrogen cyanide from coke oven gas. For cyanide solutions, the reaction was originally investigated by Wernlund and Zunick (1940). Luthy et al (1977) and Luthy and Bruce (1979) studied such transformations in coke plant and coal gasification plant effluents. International Environmental Consultants (1979 and 1981) investigated the use of the cyanide-polysulfide reaction for treatment of cyanide-containing wastewaters from the gold milling industry. However, no published data were available on the cyanide-polysulfide reaction in concentrated cyanide-containing wastewaters before the preliminary study by Takaoka and Ganczarczyk (1985). These experiments were conducted to investigate the cyanide-polysulfide reaction in a 2% solution (20,000 mg/L CN-) of sodium cyanide. It was found that the reaction proceeded very rapidly, both at room temperature and at 30C. It was 95% complete within 1 hour and cyanide concentrations were non-detectable within 2 weeks at a cyanide-to-polysulfide ratio of 1:2 by weight.

In a follow-up research, Ganczarczyk et al (1985) studied the cyanide-polysulfide reaction in two different wastewater streams from an electroplating operation. One wastewater was a dragout from the first rinse tank in a copper and cadmium plating process; the wastewater was a clear solution with a pH greater than 12.0. The second wastewater was a stripper solution for removal of metal plate (Cu/Ni plate stripping liquor); it was orange-red and contained a settleable yellow precipitate. The pH of the stripper solution was greater than 12.0. Sample volumes of 300-500 mL were reacted with limesulfur at cyanide to polysulfide ratios of 1:1.5 and 1:2 (w/w). Initial CN^- concentrations ranged from 11,400 mg/L to 56,200 mg/L. In each case a rapid degradation of CN^- was observed. The effective removal of CN^- occurred within 3 days for the copper/cadmium plating wastewater while

99.9% CN- removal was achieved in the copper/nickel plating wastewater within 2 days. Metal removals in these experiments were generally at the level required by municipal sewer use by-laws.

MATERIALS AND METHODS

In this work three different wastewater streams from a metal finishing shop were studied: zinc plating waste liquor (Zn/CN), cadmium plating waste liquor (Cd/CN), and copper plating waste liquor (Cu/CN). The pH in all these liquors was greater than 12.0 while cyanide concentrations ranged from 10,000 mg/L to 180,000 mg/L. A solution of potassium ferricyanide (20,000 mg/L CN) was also used to examine the effect of polysulfide on ferricyanide.

Three sources of polysulfide-sulfur were used in these experiments: limesulfur (calcium polysulfide), zinc purifier (sodium polysulfide) and calcium polysulfide produced in our laboratory from technical grade calcium oxide and sulfur. The limesulfur contained 230 g/L polysulfide-sulfur while zinc purifier contained 150 g/L and the laboratory produced polysulfide contained 200 g/L of this element.

Initial laboratory experiments were conducted in glass bottles sealed with rubber-stoppers. Later, a pilot-scale application was conducted on-site in 50 gallon drums. Samples were taken from the reactors at regular intervals, preserved and then analyzed for total cyanide (CN-), thiocyanate (SCN-) and soluble metals (cadmium, chromium, copper, iron, nickel, and zinc) contents.

The standard procedures for sample preservation were adapted from those used by Luthy et al. (1979), Luthy and Bruce (1979), and International Environmental Consultants (1981). To obtain a sample for determination of CN- or SCN-, 20 mL of the reactor contents were withdrawn in a volumetric pipette, transferred to a 200 mL volumetric flask, and diluted to the mark with distilled water. A few millilitres of a suspension of lead sub-acetate in water were added to the diluted sample to precipitate sulfides. The addition of the lead sub-acetate was stopped when the supernatant became cloudy-white, which indicated the presence of lead hydroxide. Normal sodium hydroxide solution was added to the samples in measured quantities during the sulfide precipitation process to maintain a pH range of 10 to 11. The lead sulfide precipitate was immediately separated from the sample by filtration under vacuum through a glass fiber filter. The filtrate was collected and its pH increased to greater than 11.0 with sodium hydroxide solution. The treated samples were stored in the dark at 3oC.

The method of CN- determination was adapted from the method of Knechtel and Conn as cited by Conn (1981). This method is similar to the acid reflux/distillation method in "Standard Methods" (1980) with an argentometric titration finish. The method adopted for SCN- determination was based on mercuric titrimetry after Vogel (1960), using 0.1 N mercuric sulfate. An excess of iron alum (ferric ammonium sulfate) was added to the sample under acidic conditions to produce the characteristic deep red color of ferric thiocyanate. After mercuric titration, the mercuric ion replaces the ferric ion and the red color gradually disappears, leaving the solution colorless. Polysulfides were determined with a procedure developed by Schulek as cited by Karchmer (1970). This method was based on the reaction of alkali cyanides with the soluble polysulfides under anaerobic conditions to form one SCN- ion for every atom of polysulfide-sulfur. The cyanide-polysulfide reaction was carried out in a boric acid medium. Hydrogen sulfide and excess hydrogen cyanide were driven off by boiling the acidifed solution; the SCN- and the thiosulfate remained unaffected in solution. The determination of SCN- and thiosulfate was performed by indirect iodometric titration with a starch indicator.

The analysis for soluble metals was performed using an atomic absorption spectrophotometer. A measured volume of sample filtered by a 0.45-μ membrane filter was boiled with 20 mL of concentrated nitric acid to decompose the residual cyanide that could interfere with the metals analysis. After cooling, the sample was diluted to 250 mL with distilled water and subjected to atomic absorption spectrophotometry.

EXPERIMENTAL PROGRAM AND RESULTS

The first sets of experiments were designed to determine the general effectiveness of calcium polysulfide and sodium polysulfide in the reaction with cyanide. A wastewater containing 64,900 mg/L CN- was reacted with both types of polysulfide at various CN:poly-S^o ratios. The obtained results are presented in Tables 1 and 2.

The second set of experiments involved the application of limesulfur to the three types of wastewater to determine optimum dosages and effectiveness. Results of a cyanide to polysulfide ratio of 1:2 by weight are listed in Tables 3, 4 and 5 and presented in Figures 1, 2 and 3. The results for the studied cyanide to polysulfide ratios of 1:1.5 by weight are not included in this report.

The next experiments were designed to determine the effect of dilution on the reaction of cyanide and polysulfide. Here, samples of the three wastewaters were diluted to two or three times their initial volume, and then reacted with calcium polysulfide at CN:poly-S^o ratios of 1:1.5 and 1:2 by weight. Results for dilute zinc/cyanide wastewater are listed in Table 6 and presented in Figure 4.

Table 1: Decrease of Cyanide Concentrations (mg/L) With the Application of Calcium Polysulfide As A Reagent

Ratio of CN: Poly-S (w/w)	Duration of the Experiment					
	0	0.5 hr.	1 day	2 day	3 day	4 day
1:1	64,900.0	2,125.0	2,200.0	2,437.5	2,412.5	2,050.0
1:1.5	64,900.0	125.0	75.0	12.5	25.0	0
1:2	64,900.0	12.5	12.5	0	0	0

Table 2: Decrease of Cyanide Concentrations (mg/L) with the Application of Sodium Polysulfide

Ratio of CN: Poly-S (w/w)	Duration of the Experiment					
	0	0.5 hr.	1 day	2 day	3 day	4 day
1:1	64,900.0	2,850.00	2,675.0	2,400.0	2,125.0	2,125.0
1:1.5	64,900.0	100.0	500.0	137.5	25.0	25.0
1:2	64,900.0	50.0	75.0	0	0	0

Table 3: Concentration of Pollutants in the Liquid Phase Obtained During the Treatment of Cadmium Cyanide Electroplating Solution at the Cyanide/Polysulfide Ratio of 1:2

Pollutants in mg/L	Duration of the Experiments					
	Initial	1 day	7 day	14 day	21 day	28 day
CN	65750.0	62.5	0	0	0	0
Fe	704.8	631.5	660.7	648.7	678.0	357.0
Zn	217.5	10.5	4.0	5.6	5.6	4.0
Cu	287.5	95.7	23.2	9.3	14.2	12.7
Ni	28.3	5.5	4.5	7.1	5.5	4.5
Cd	4212.5	4.5	4.7	4.0	5.3	3.2
Cr	24.8	3.0	1.0	1.3	0.5	0.5

Table 4: Concentration of Pollutants in the Liquid Phase Obtained During the Treatment of Copper Cyanide Electroplating Solution at the Cyanide/Polysulfide Ratio of 1:2

Pollutants in mg/L	Duration of the Experiments					
	Initial	1 day	7 day	14 day	21 day	28 day
CN	56075.0	62.5	0	0	0	0
Fe	416.2	485.0	396.0	452.0	425.0	356.0
Zn	2.5	0.7	0	0	0.5	1.0
Cu	35050.0	131.0	49.0	37.5	42.0	10.1
Ni	5.5	1.4	0.8	1.2	0.6	0.6
Cd	0.5	0.5	0.3	0	0	0
Cr	2.0	1.5	1.0	1.2	0.7	0

Table 5: Concentration of Pollutants in the Liquid Phase Obtained During the Treatment of X-Pert Zinc Cyanide Electroplating Solution at the Cyanide/Polysulfide Ratio of 1:2

Pollutants in mg/L	Duration of the Experiments					
	Initial	1 day	7 day	14 day	21 day	28 day
CN	7900.0	175.0	125.0	0	0	0
Fe	855.0	651.0	509.0	656.0	704.0	571.0
Zn	5325.0	132.0	2.5	3.0	1.8	2.1
Cu	6.5	2.7	0.5	0	0.3	0.5
Ni	2.5	0.8	0.4	0.6	0.4	0.4
Cd	0.5	0.3	0.3	0	0	0
Cr	4.5	2.2	0.5	0.7	0	0

It was also desired to determine the feasibility of producing calcium polysulfide on-site. Several experiments were performed in which the amounts of CaO, S, and water were varied. The reaction time was also varied. The experimental conditions and results are given in Table 7.

The final series of experiments concerned the pilot-scale application of this technology. One experiment involved the application of 20 litres of calcium polysulfide (produced in the laboratory at the University of Toronto) to 110 L of zinc/cyanide wastewater. The initial cyanide concentration was 17,900 mg/L and the polysulfide contained over 200 g/L polysulfide sulfur (CN:poly-s^o ratio of 1:2). Another pilot-scale test involved an application of 61 litres of zinc purifier containing 150 g/L polysulfide-sulfur, to 25 litres of cadmium/cyanide wastewater. The initial cyanide concentration was 181,000 mg/L (CN:poly-S^o ratio of 1:2). The results of these two experiments are presented in Tables 8 and 9 and in Figures 5, 6, 7 and 8.

Because of the apparent interference from ferricyanide (Luthy and Bruce, 1978), a series of experiments were carried out to determine the effect of polysulfide on ferricyanide. Varying amounts of sodium-polysulfide were added to a solution of potassium ferricyanide to obtain CN:poly-S^o ratios of 1:1.5, 1:2, and 1:2.5. The results are presented in Table 10.

Other work done includes:

1. Determination of the reaction heat in different spent cyanide liquors at various cyanide to polysulfide ratios.
2. Preliminary tests on the application of various reagents to remove residual polysulfide from the treated cyanide liquors after completion of the polysulfide reaction.
3. Preliminary leaching tests on the precipitates formed in the cyanide-polysulfide reaction.

The values of the reaction heat were determined by measuring the temperature rise in the laboratory reaction apparatus. In each case, 50 mL

Table 6 - Effect of Dilution on the Concentrations of Cyanide (mg/L) in the Liquid Phase with the Application of Calcium Polysuflide

Ratio of CN:Poly-S^o (w/w)	Duration of Experiments (days)					
	0	1	4	7	14	21
1:1.5	3625.0	125.0	62.5	31.3	0	0
1:2	3625.0	125.0	96.2	31.3	0	0
1:1.5	7900.0	187.5	125.0	0	0	0
1:2	7900.0	175.0	125.0	0	0	0

Table 7 - Calcium Polysulfide Production (Experimental Results and Conditions)

Sample	Components			Reaction Time (hrs)	Final Volume (mL)	Polysulfide Content
	CaO (g)	S (g)	H_2O (mL)			
1	20	70	300	24 (reflux condenser)	300	5% ± 1%
2	20	60	200	4	55	22% ± 1%
3	20	70	200	4-5	96	23% ± 1%
4	30	70	300	5	127	9% ± 1%
5	20	60	400	7	130	16% ± 1%

* Note: all samples were continually stirred throughout boiling time with a magnetic stirrer.

Table 8 - Liquid Phase Pollutant Concentrations (mg/L) in the Treatment of Zinc/Cyanide Spent Liquor (initial cyanide to polysulfide ratio of 1:2)

	Duration of Experiments (days)						
Pollutants	Initial	1	3	6	13	23	30
CN	17900.0	1125.0	425.0	225.0	100.0	300.0	350.0
SCN	0.0	21140.0	12550.0	11620.0	4650.0	11620.0	6970.0
Fe	2600.0	220.0	140.0	100.0	120.0	120.0	120.0
Zn	9000.0	140.0	540.0	20.0	20.0	20.0	16.0
Cu	50.0	8.0	10.0	6.0	4.0	2.0	0.0
Cd	0.3	0.0	0.0	0.0	0.0	0.0	0.0
Cr	5.0	5.0	4.0	4.0	2.0	2.0	2.0
Ni	20.0	12.0	20.0	14.0	2.0	2.0	2.0

Table 9 - Liquid Phase Pollutant Concentrations (mg/L) in the Treatment of Cadmium/Cyanide Spent Liquor (initial cyanide to polysulfide ratio of 1:2)

	Duration of Experiments (days)					
Pollutants	Initial	1	3	6	9	16
CN	181000.0	63.0	10.0	15.0	12.5	10.0
SCN	0.0	6970.0	3950.0	1160.0	2556.0	860.0
Fe	1400.0	6.2	2.5	0.8	2.0	1.9
Zn	940.0	0.6	0.6	0.7	2.0	0.8
Cu	660.0	0.8	1.0	1.1	1.2	0.6
Cd	9800.3	0.4	0.3	0.5	0.4	0.3
Cr	15.0	2.0	3.1	2.4	2.8	1.6
Ni	36.0	3.8	3.0	2.4	1.8	1.4

Table 10 - Concentration of Pollutants (mg/L) in the Liquid Phase Obtained During Treatment of Potassium Ferricyanide with Sodium Polysulfide

No.	Ratio of CN:poly-S^o (w/w)	Pollutants (mg/L)	Duration of Experiments (days)			
			0	1	3	9
1	1:1.5	CN	20000	12000	10200	7750
		Fe	7155	3000	1800	1000
		SCN	0	0	0	0
2	1:2	CN	20000	7800	5000	8750
		Fe	7155	800	600	1400
		SCN	0	0	0	0
3	1:2.5	CN	20000	9500	1700	2250
		Fe	7155	1000	800	400
		SCN	0	0	0	0
4	1:2	CN	200	163	nd	125
		Fe	72	26	nd	20
		SCN	0	0	nd	0

*note: nd = not done

Table 11 - Estimation of Reaction Heat

Sample Source	Cyanide Amount (g)	Initial CN:Poly-S°	Initial Temperature (°C)	Peak Temperature (°C)	Maximum Temp. Rise (°C)	Heat of Reaction (cal/g (CN))
Zinc-Plating Solution	0.3500	1:1.5	27.49	30.36	2.87	410.0
		1:2	28.27	31.24	2.97	424.3
Cadmium-Plating Solution	0.6103	1:1.5	25.86	30.83	4.97	407.2
		1:2	26.80	31.96	5.16	422.7
Copper-Plating Solution	1.1719	1:1.5	26.67	31.79	5.12	218.4
		1:2	25.80	31.14	5.34	227.8
Copper-Plating Solution	0.9354	1:1.5	26.50	30.00	3.50	187.1
	2.8013		26.80	36.30	9.50	169.6
KCN Solution	0.2000	1:2	27.04	28.70	1.66	415.0
			27.01	28.73	1.72	430.0

* Specific heat of these solution is assumed to be 1 cal/g.°C.

Table 12 - Removal of Excess Polysulfide from the Cadmium Electroplating Solution

Test No.	1	2	3	4	5
Volume of Sample (mL)	10	10	10	10	10
Volume of 10% $FeSO_4 \cdot 7H_2O$ sol. Added (mL)	0	1	3	4	5
Poly-S^o concentration (mg/L)	10740.1	4618.2	961.8	480.9	705.3
Removal Efficiency (%)	0	43	91	95.9	93.4

Table 13 - Metal Ion Concentrations in the Leachate from the Zinc Electroplating Solution Precipitate (mg/L)

		Duration of Leaching				
		1 day	3 day	7 day	9 day	15 day
Fe	A	nd	nd	14.0	6.8	13.0
	B	nd	nd	11.6	4.6	11.2
Zn	A	nd	0	0.2	0	0
	B	nd	6.6	5.1	0	4.8
Cu	A	nd	nd	0.8	1.0	0.8
	B	nd	nd	0.6	1.0	0.6
Ni	A	nd	nd	0.4	0	0
	B	nd	nd	0.2	0.2	0
Cd	A	nd	nd	0	0	0
	B	nd	nd	0	0	0
Cr	A	nd	nd	0	0	0
	B	nd	nd	0	0	0

Note: A represents the sample of precipitate + fly ash
B represents the sample of precipitate only
nd: not done

Table 14 - Metal Ion Concentrations in the Leachate from the Copper Electroplating Solution Precipitate (mg/L)

		Duration of leaching		
		1 day	3 day	9 day
Fe	A	0.6	0	0.8
	B	0.2	0.2	0.8
Zn	A	0.2	0.4	0.4
	B	0.2	0.2	0.2
Cu	A	2.6	2.0	0.6
	B	1.0	1.0	0.8
Ni	A	0.4	0.2	0.2
	B	0.4	0.4	0
Cd	A	0	0	0
	B	0	0	0
Cr	A	0	0	0
	B	0	0	0

Note: A represents the sample of precipitate + fly ash
B represents the sample of precipitate only

Table 15 - Metal Ion Concentrations in the Leachate from the Cadmium Electroplating Solution Precipitate (mg/L)

		Duration of leaching		
		1 day	3 day	9 day
Fe	A	9.6	6.8	6.6
	B	6.0	4.6	4.0
Zn	A	0.2	0	0
	B	0.2	0	0
Cu	A	0.8	1.0	0.8
	B	0.8	1.0	0.8
Ni	A	0.6	0	0.4
	B	0.8	0.2	0.6
Cd	A	0	0	0
	B	0.2	0	0
Cr	A	0	0	0
	B	0	0	0

Note: A represents the sample of precipitate + fly ash
B represents the sample of precipitate only

samples were used, and the reactor was continually agitated to ensure a uniform temperature distribution throughout the vessel. The obtained data are listed in Table 11.

Removal of residual polysulfide from the treated liquors by the additions of $FeSO_4$ was examined by taking 10 mL samples of the cadmium/ cyanide-polysulfide reaction product and adding to it 1, 3, 4, 5, 7 and 10 mL of 10% $FeSO_4 \cdot 7H_2O$. The resulting data are presented in Table 12.

The procedure employed in the precipitate leaching tests was as follows: The precipitate was first dried in an oven at 103°C. One gram of the dried precipitate was added to 100 mL of distilled water. To some samples, 1 g of fly ash was also added in a slurry of its original solution. All samples were then shaken, and dissolved metals concentrations were determined at regular intervals. The results are presented in Tables 13, 14 and 15.

DISCUSSION

There was no significant difference in efficiency between calcium polysulfide and sodium polysulfide applied for cyanide liquors treatment. Both types of polysulfide were effective at reducing cyanide concentrations at cyanide to polysulfide ratios of 1:2 and 1:1.5. Because calcium polysulfide could be presumably cheaper if produced in bulk quantities, it was chosen as the preferred alternative. A preliminary economic analysis revealed that calcium polysulfide could be produced at 40% of the purchase cost. Current prices for limesulfur (bulk) are $1.50/Litre @ 230 g/L polysulfide sulfur. Zinc purifier is available for $1.05/Litre, but it contains only 150 g/L polysulfide sulfur. So, for 1 kg polysulfide sulfur (for example) the costs are as follows:

Limesulfur (calcium polysulfide):	4.3 L @ $1.50/L = $6.53
Zinc Purifier (sodium polysulfide):	6.67 L @ $1.05/L = $7.00

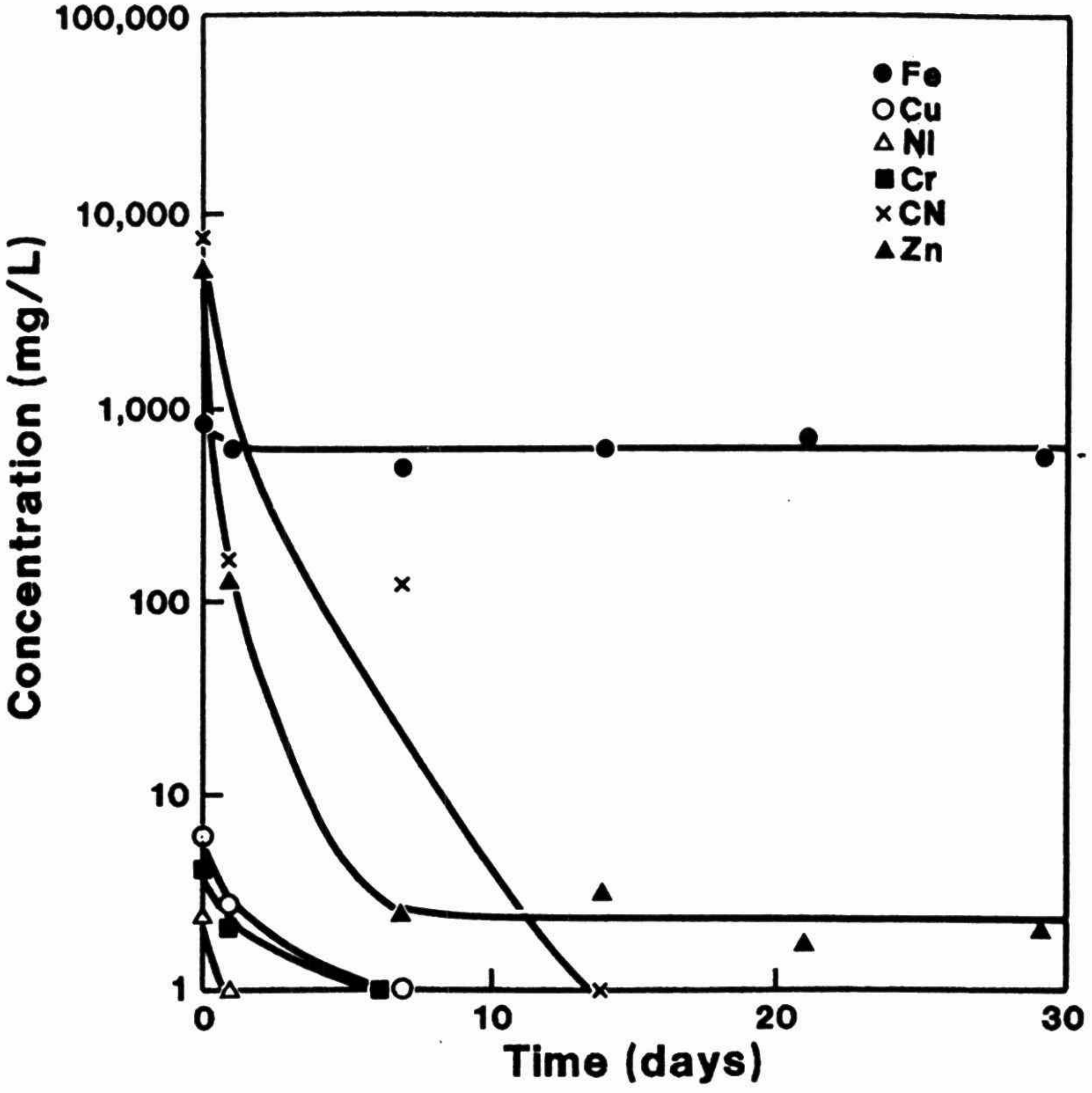


Figure 1 - Application of calcium polysulfide in the treatment of a Zinc/Cyanide spent liquor at a CN:Poly-So Ratio of 1:2.

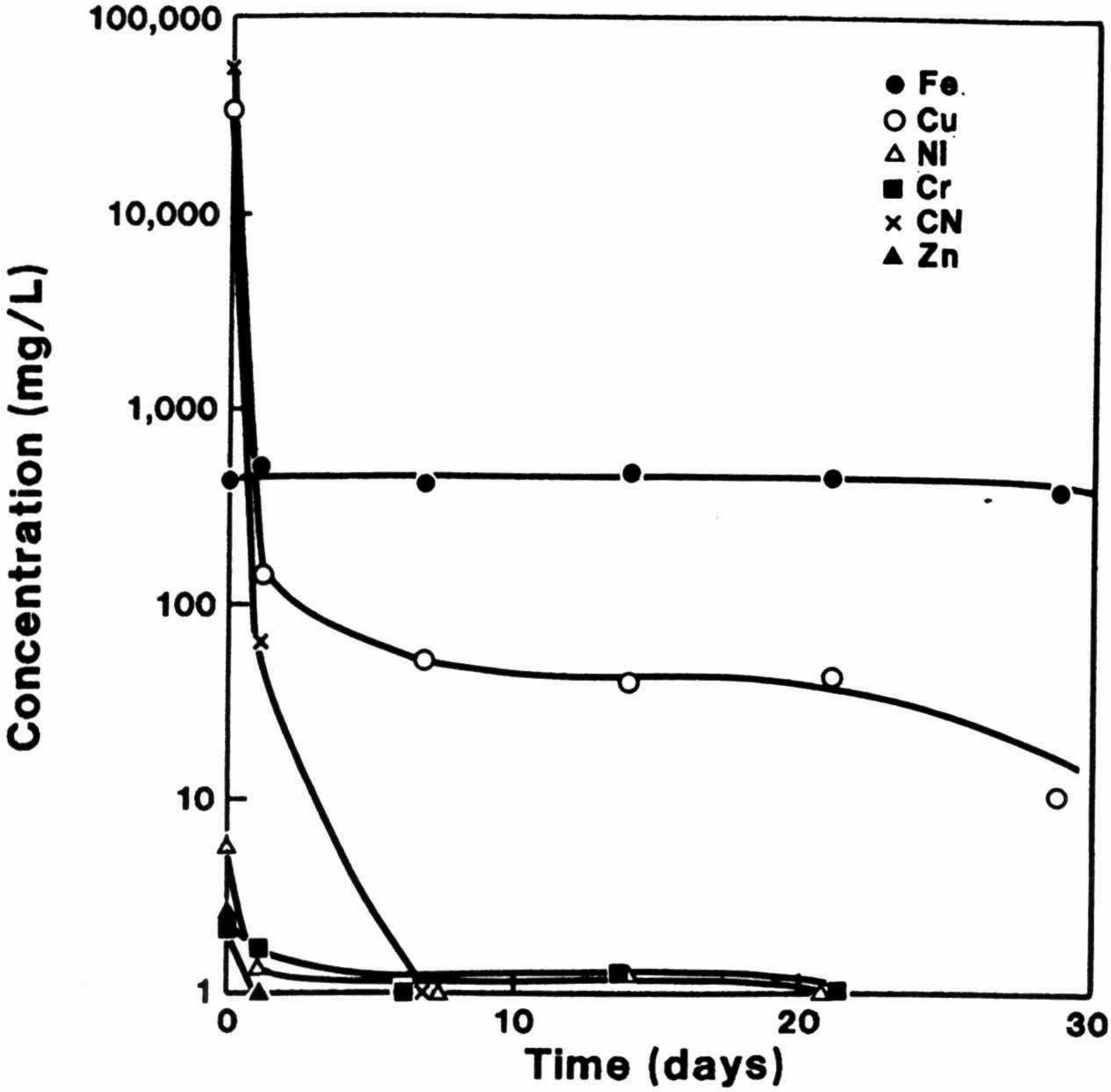


Figure 2 - Application of calcium polysulfide in the treatment of a Copper/Cyanide spent liquor at a CN:Poly-S^o ratio of 1.2.

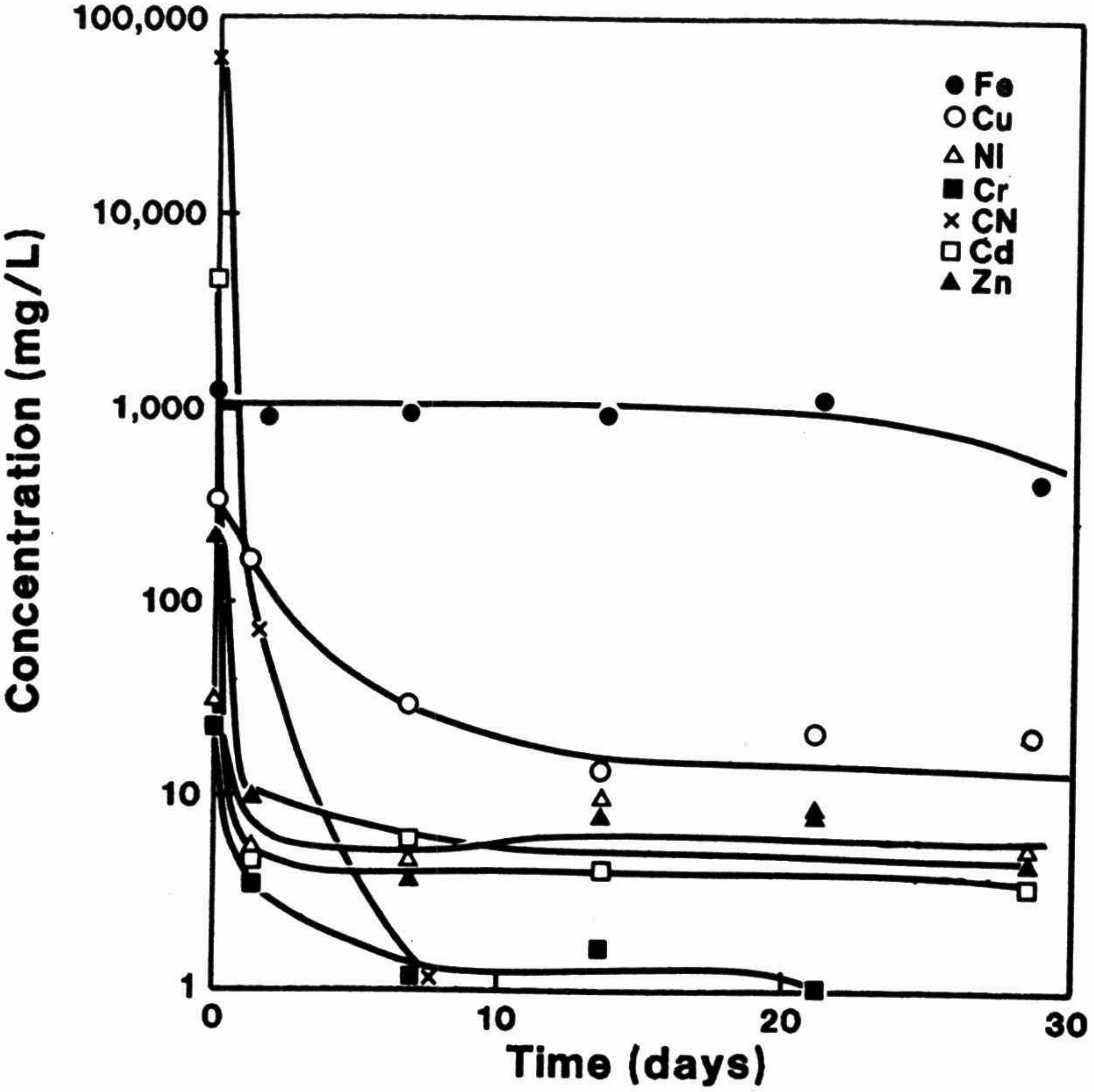


Figure 3 - Application of calcium polysulfide in the treatment of a Cadmium/Cyanide spent liquor at a CN:Poly-S^o ratio of 1:2.

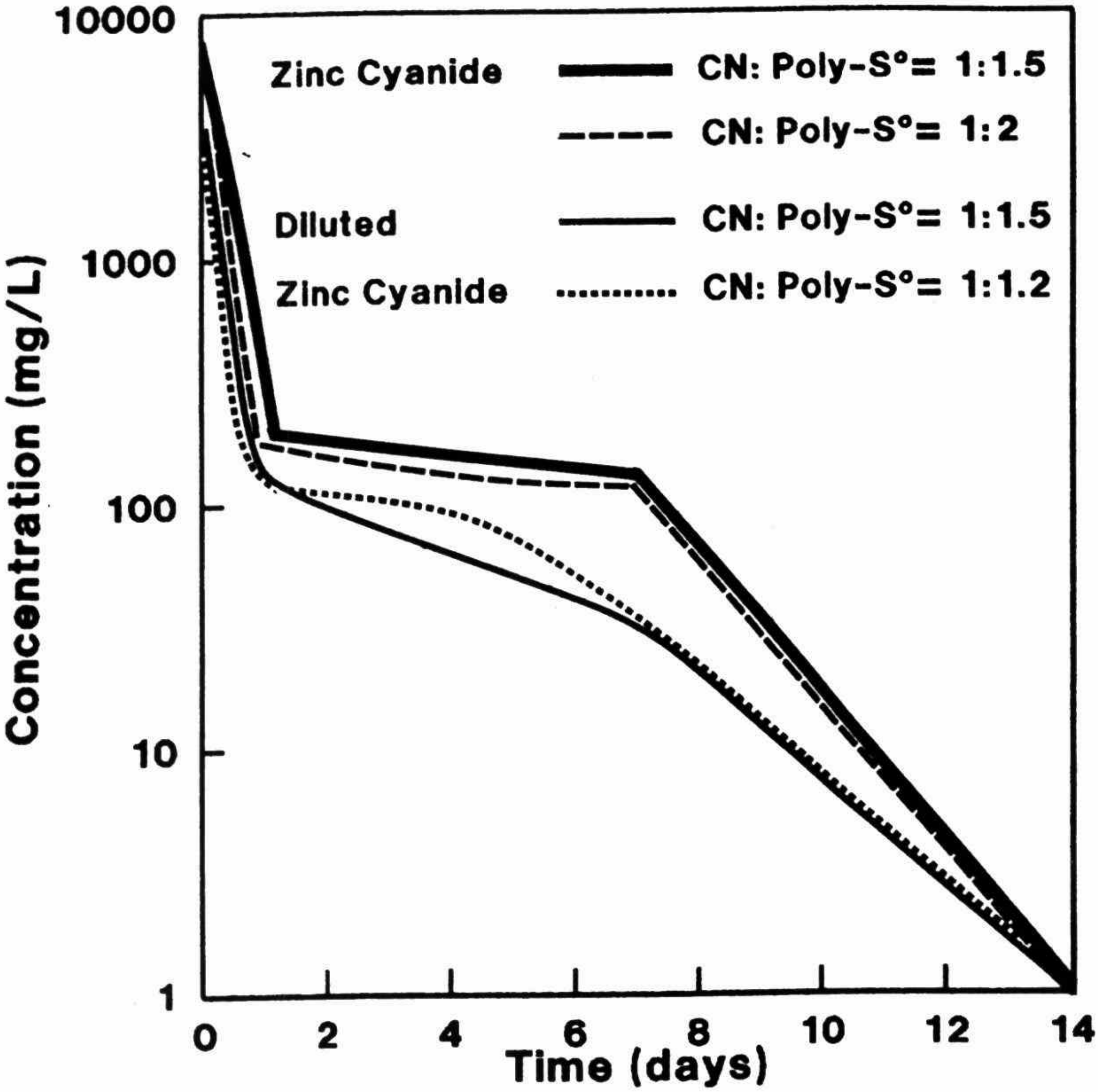


Figure 4 - Effect of dilution on cyanide removal by the Application of calcium polysulfide.

It must be noted, however, that zinc purifier is readily available at most metal finishing shops since it is commonly used in day-to-day operation as a plating bath purifier.

The preliminary tests on the three studied wastewaters showed rapid degradation of CN-. Cyanide was reduced to non-detectable levels within 7 days for both the cadmium/cyanide and copper/cyanide wastewaters at cyanide to polysulfide ratios of 1:2. The zinc/cyanide wastewater required two weeks to bring the cyanide levels to the non-detectable range i.e. < 1 mg/L.

Metal ion removal was also quite effective in all cases. Most metals were reduced to concentrations less than 10 mg/L (after 28 days) with the exception of iron and copper. However, the eventual copper levels were only slightly above 10 mg/L for the cadmium/cyanide and copper/cyanide wastewaters. But the iron content remained at concentrations above 350 mg/L in all the studied cases. In the zinc/cyanide wastewater, iron remained at a concentration of 570 mg/L. It appears that iron, while being difficult to remove, also hinders the cyanide-polysulfide reaction. This hypothesis was further substantiated by the pilot-scale application results.

Dilution did not have a significant effect on the cyanide-polysulfide reaction. After 1 day, 96.5% of the cyanide was removed in the diluted sample, while 97.6% was removed in the undiluted sample. The diluted sample did, however, take longer to reach undetectable cyanide concentrations.

Experiments showed that calcium polysulfide can be produced by the user. Concentrations as high as 23% polysulfide-sulfur were attained after 4-5 hours of boiling the lime suspension with elemental sulfur. Based on these results, 20 litres of 20% calcium polysulfide were produced in the laboratory at the University of Toronto. This was then used to treat 110 litres of zinc/cyanide wastewater in the first pilot-scale test (see Figures 7 and 8).

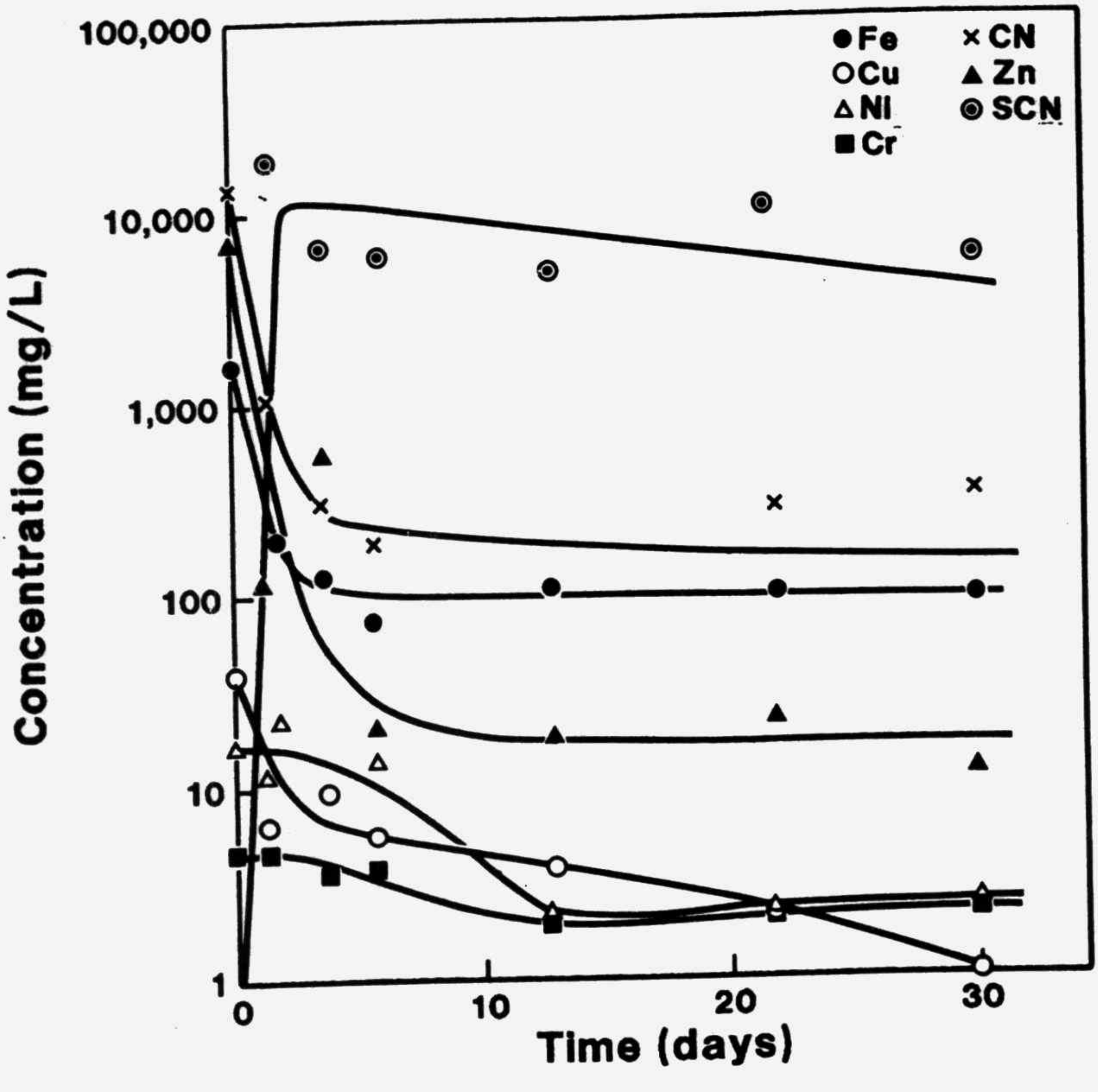


Figure 5 - Pilot-Scale application of produced calcium polysulfide in the treatment of Zinc/Cyanide spent liquor at a CN:Poly-S^o ratio of 1:2.

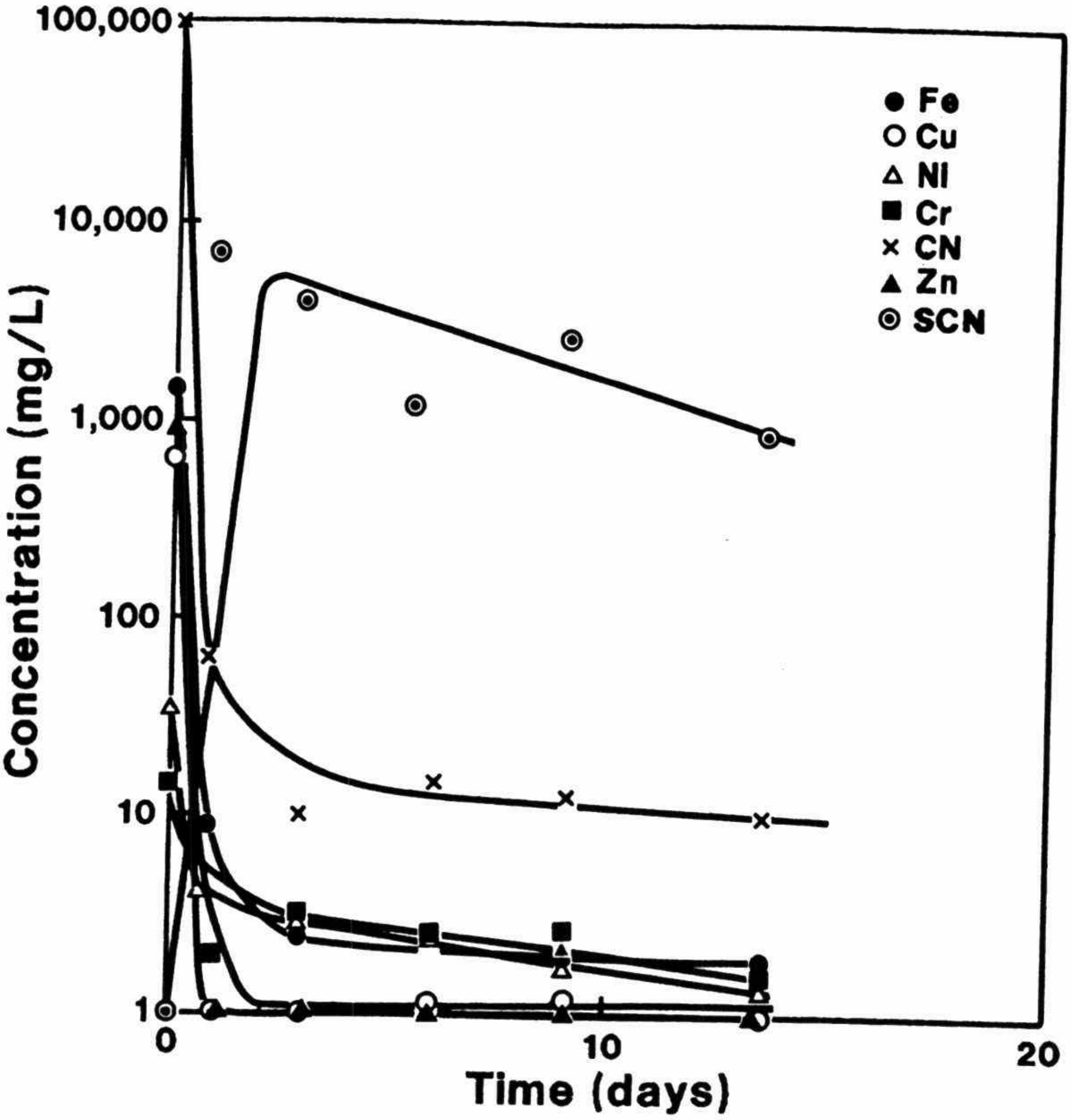


Figure 6 - Pilot-Scale application of purchased sodium polysulfide in the treatment of Cadmium/Cyanide spent liquor at a CN:Poly-So ratio of 1:2.

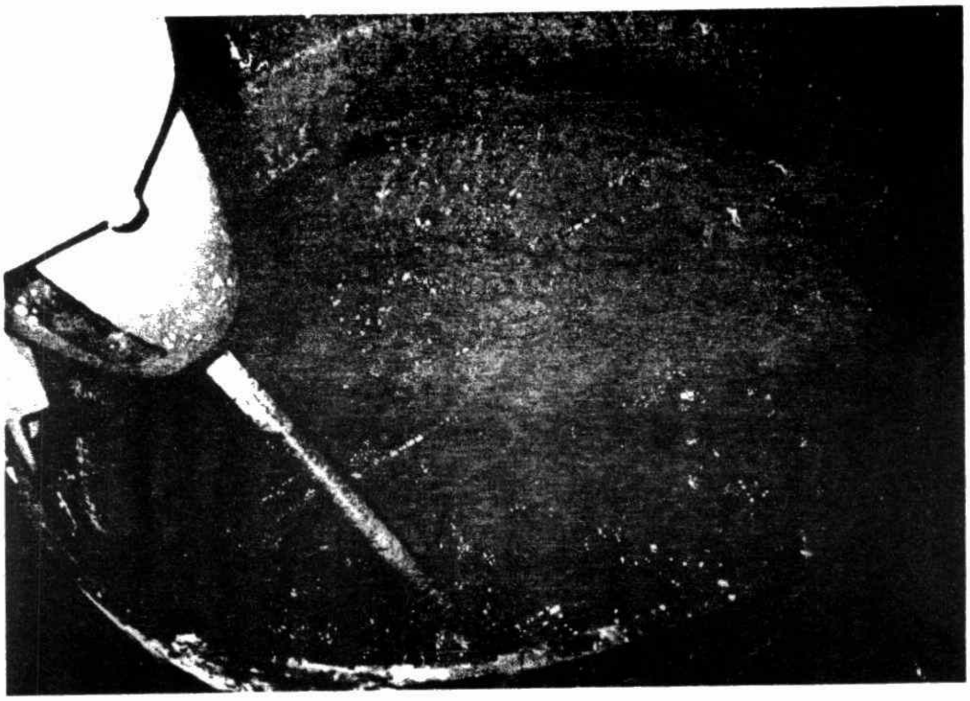


Figure 7 - Reaction of Zinc/Cyanide Wastewater with Produced Calcium Polysulfide.

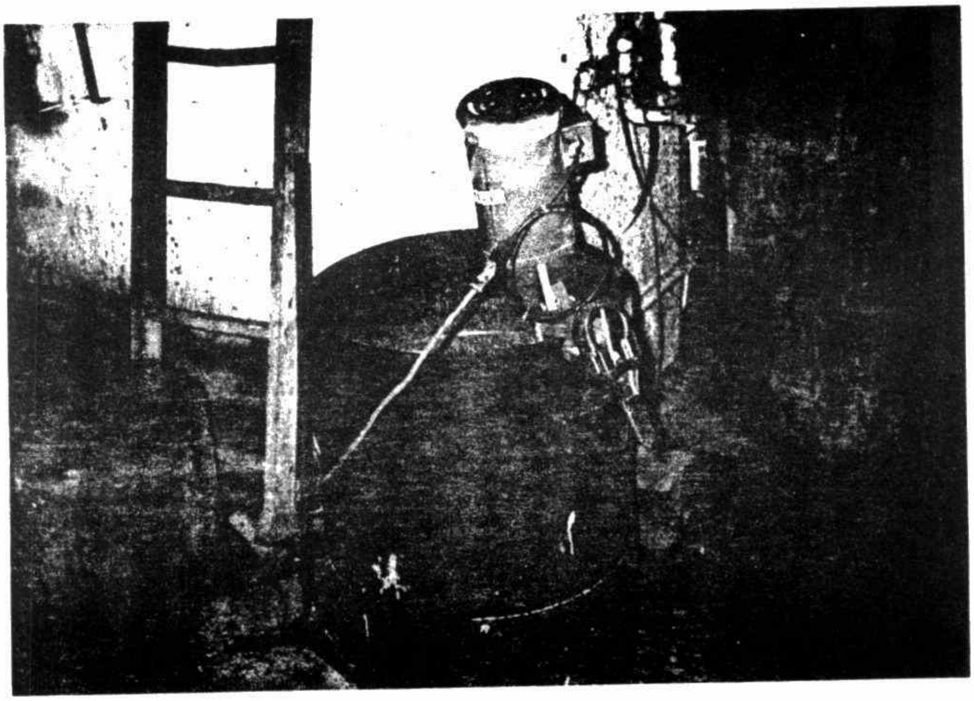


Figure 8 - Reaction Vessel Used in Pilot-Scale Application of Polysulfide.

Cyanide concentrations were reduced by 97.6% within 3 days. A slight decrease over the next few weeks was observed but complete removal was not attained. It was hypothesized that this was due to the high initial iron concentrations. This was somewhat substantiated by the second pilot-scale test. Along with the decreasing cyanide concentrations, an initial thiocyanate increase was noted. As it was observed by Ganczarczyk et al (1985), the thiocyanate concentration then decreased over the duration of the test.

As with the preliminary tests, most metals were reduced to concentrations below 10 mg/L. The exceptions here were Zn and Fe. The lowest zinc concentrations were determined at 16 mg/L, while iron content remained steady at 120 mg/L. Considering the very high initial iron concentration (2600 mg/L) the iron removal achieved was quite good. It was postulated that perhaps a further addition of polysulfide might take the reaction to completion. This was not found to be the case, however. Experiments not cited here revealed that no additional cyanide removal had taken place.

The second pilot-scale application of polysulfide was somewhat more successful than the first one. Cyanide concentrations were reduced by 99.9% after one day. As with the first test, cyanide concentrations could not be brought down to undetectable levels. Thiocyanate also displayed similar characteristics to those in the first test, i.e. initial increase followed by a continual decrease. The peak thiocyanate concentrations were, however, considerably less (7,000 mg/L vs 21,000 mg/L). A temperature rise of 12°C was noted at the beginning of the experiment.

Metal ion removal was considerably more effective in the second pilot-scale test. All metals (including iron) were brought to concentrations less than 5 mg/L within 10 days. The initial iron concentration, however, was much lower in the second test (1,400 mg/L vs 2,600 mg/L). This increased removal in the cadmium/cyanide wastewater (compared to the zinc/cyanide wastewater) was, however, not unexpected. The initial tests also showed some difficulty in dealing with the zinc/cyanide wastewater. As it was mentioned earlier in the discussion, it was hypothesized that the differences in removal efficiencies may have been due to the iron concentrations.

To further examine this possibility, the potassium ferricyanide-polysulfide tests were conducted. In all cases, cyanide concentrations were reduced but no thiocyanate was formed in this reaction. This further confirms the results of Luthy & Bruce (1978). It seems that some further cyanide-metal complexation occurs with the addition of polysulfide. No further tests were done on this phenomenon.

The values of the reaction heat for both the zinc/cyanide and cadmium/cyanide wastewaters were found to be about 400 cal/g (CN). The temperature rise in the mixture thus depends on the amount of cyanide present. In the second pilot-scale test, a rise of 12oC (from 27oC to 39oC) was noted at the beginning of the test. Considering that the initial cyanide concentration was 181,000 mg/L, however, no problems in this regard are foreseen.

Since polysulfide is known as a very active substance, it may cause problems to the receiving water body if discharged without further treatment. Removal of residual polysulfide is therefore of some concern. Experiments showed that the addition of $FeSO_4$ can effectively remove residual polysulfide. Since $FeSO_4$ is usually readily available in metal finishing shops (i.e. it is produced in the recovery of sulfuric acid from spent pickle liquors), the process itself is inexpensive. The procedure also results in a decrease in pH which makes the effluent easier to discharge.

The preliminary leaching tests on the precipitates show that the metal ion concentrations in the leachate are quite low. This is primarily due to the very low solubilities of metal sulfides. The addition of flyash reduced the metal ion concentrations in some instances. This is attributed to the sorption capacity and ion exchange capability of the flyash. Further tests on the precipitates formed in the cyanide-polysulfide reaction are planned.

CONCLUSIONS

This study was conducted to examine the effectiveness of the cyanide-polysulfide reaction in treating concentrated cyanide liquors that contained soluble metal compounds presumably in the form of metal-cyanide complexes. The primary objective was to produce an effluent acceptable for discharge to municipal sanitary sewer systems. Although many questions of scientific interest were left to be resolved, the following conclusions were made:

- There is effectively no difference between calcium and sodium polysulfide as a reagent for this treatment.
- Dilution has little effect on cyanide and metal ion removals; the reaction is actually more rapid at higher cyanide cincentrations.
- Calcium polysulfide can be easily produced on-site at practical ranges of concentration.
- Over 95% of cyanide can be effectively removed from concentrated spent liquors with the addition of polysulfide at CN:poly-s^o ratios only slightly greater than stoichiometric requirements (i.e.> 1:1.23).
- Metals can be reduced to concentrations of less than 10 mg/L with the exception of iron when it is present in very high initial concentrations.

- SCN- produced by CN- conversion was partially lost during the process.
- Polysulfide does reduce cyanide concentrations in ferricyanide but does not form thiocyanate in this reaction.
- The cyanide/polysulfide reaction is mildly exothermic (about 400 cal/g CN).
- Residual polysulfide is easily removed from the reaction product by the addition of $FeSO_4$. Removal efficiencies are greater than 95%.
- Very little metal ion leaching can be expected from the precipitate formed in the reaction between cyanide liquors and polysulfide.

It is believed that the cyanide-polysulfide reaction provides a safe, effective, and practical means of detoxifying highly concentrated waste cyanide solutions. The simplicity of the process and the ready availability of the polysulfide reagent make this technology appropriate for use in some small electropolating shops or developing countries.

Treatment of Landfill Leachate By Spray Irrigation - Muskoka Lakes

R.A. McBride[1] A.M. Gordon[2] P.H. Groenevelt[1]

Introduction

The Muskoka Lakes sanitary landfill site (lots 21, 22 and 23, Concession 1, Medora Ward, Township of Muskoka Lakes, District Municipality of Muskoka) is the first known location in Ontario to have installed a leachate collection and spray irrigation disposal facility. The system at the present time consists of i) a leachate collection trench situated downslope from the capped landfill, ii) two settling lagoons where some limited aeration treatment is achieved, and iii) a network of 72 spray irrigation nozzles distributing partially treated leachate over three areas totalling approximately 4.3 ha in a mixed hardwood forest (see Figure 1). Spray irrigation was selected as an engineering solution to the leachate generation problem of this site since a suitable alternative disposal site for source removal though excavation and transport could not be found within the municipality (M.M. Dillon, 1980; Totten, Sims, Hubicki Assoc. Ltd., 1983).

At current rates, 2.4×10^7 ℓ or more of leachate will be generated and collected annually at this landfill for decades to come. Given the maximum current disposal capacity of about 2.0×10^7 $\ell \cdot yr^{-1}$ under ideal conditions between April and October at this site (i.e. spraying not abated due to rainfall), even the current scale of operations may provide inadequate over the long-term (Gartner Lee Assoc. Ltd., 1984). Little published research exists on leachate disposal and attenuation through spray irrigation on land which is applicable to Ontario conditions. This would suggest that unforeseen problems may arise in the future which would preclude leachate application at the present rates and reduce the efficiency and acceptability of this disposal method in both economic and environmental terms.

A one year research study was initiated in 1986, with the financial support of the Ontario Ministry of the Environment, which constitutes the first phase of a longer term (3 year) research plan on this method of leachate disposal in Ontario. Consistent with the above concerns, the broad study objective is to evaluate leachate spray irrigation as a cost-

---

[1] Dept. of Land Resource Science, University of Guelph; [2] Dept. of Environmental Biology, University of Guelph. The authors gratefully acknowledge the financial support of the Ontario Ministry of the Environment through research grant 244-RR.

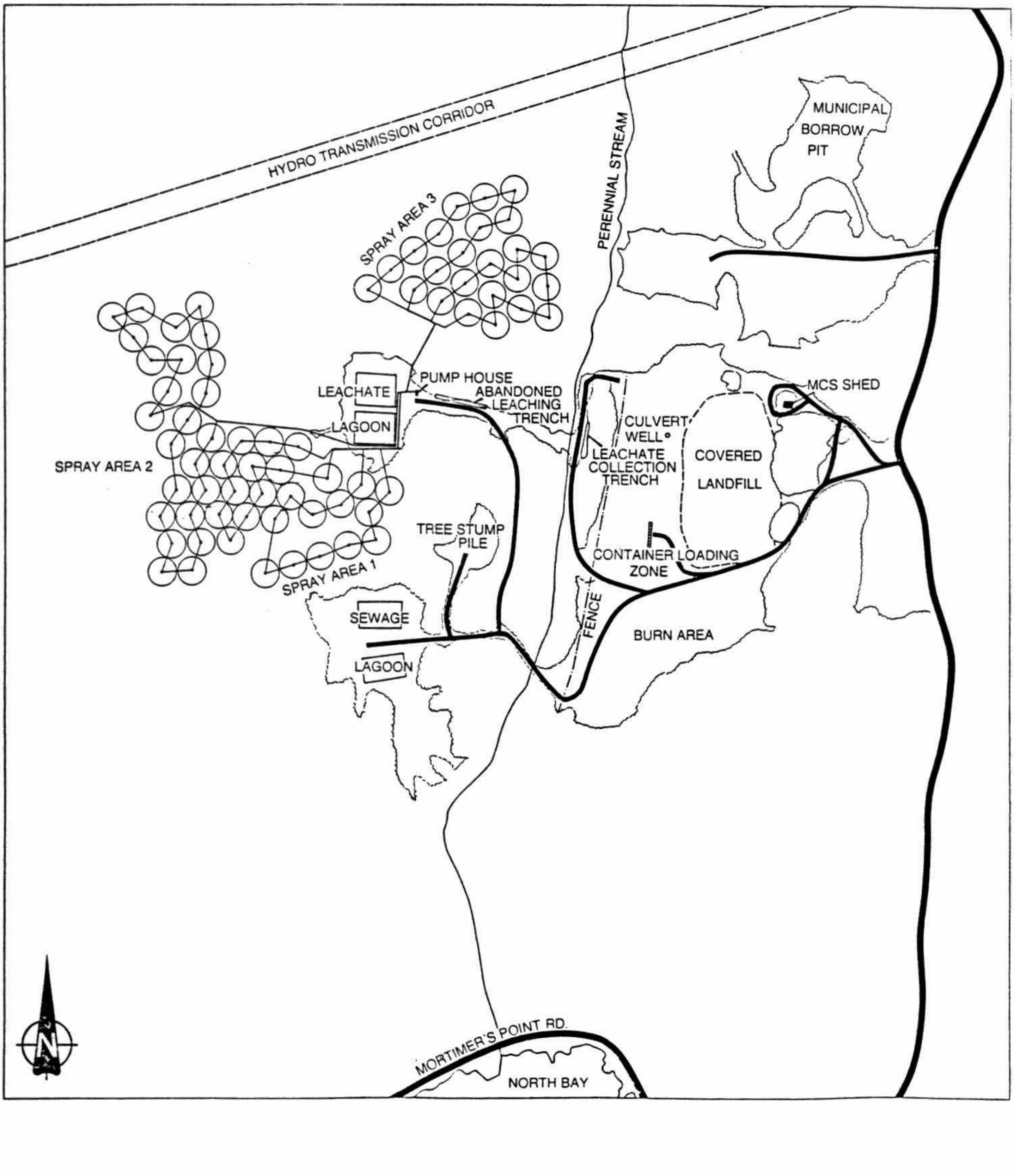


Figure 1. The Muskoka Lakes sanitary landfill site.

effective, environmentally-sound, and long-term solution to the Muskoka Lakes sanitary landfill seepage problem. At the time of writing, the project was only at the midway point of its 12-month duration. This manuscript, therefore, constitutes a progress report only and will deal more with the study approach taken rather than definitive results and conclusions.

Literature Review

Spray irrigation systems are designed to recycle landfill leachate back into the soil-vegetation ecosystem in such a way that the maximum degree of renovation and attenuation of contaminants is effected before the leachate re-enters the hydrologic cycle as deep drainage within the land disposal area. Through the processes of soil infiltration and interflow in the unsaturated zone, the leachate will be physically dispersed and diluted to varying degrees. Furthermore, inorganic compounds will be chemically precipitated or adsorbed on soil colloid exchange sites and the organic contaminants will be decomposed by the soil microbial population. Both of these chemical processes will contribute both macro- and micro-nutrients and other elements available for plant uptake and concentration in biomass. An additional design criterion is that, before the leachate reaches the groundwater table and flow systems, evapotranspiration be maximized and overland leachate flow (surface runoff) be strictly controlled or avoided. Thus, both biological and physico-chemical forms of treatment are required to encompass the broad range of leachate constituents. This is particularly true of medium aged, inactive landfills like the Muskoka Lakes site since the dominant renovation process shifts from biological to physico-chemical with time reflecting the temporal variability of leachate compounds and concentrations (Totten, Sims, Hubicki Assoc. Ltd., 1983).

A considerable body of research information exists on spray irrigation of municipal sewage wastewaters in both grass and forest ecosystems (Richenderfer et al., 1975; Sopper, 1975; Harris et al., 1976; Papadopol, 1984). Disposal of landfill leachate using similar techniques is a much more recent practice and is not widespread (Nordstedt, 1975; Menser et al., 1978). Like sewage wastewaters, landfill leachate also contains all essential plant nutrients and would seem to have good potential for recycling through ecological systems. The major obstacle to this usage is the excess concentrations of certain elements that have phytotoxic properties (i.e. iron, manganese) and of heavy metals which accumulate in plant biomass. Indeed, it has been widely observed that the direct contact of leachate with plant foliage is phytotoxic, although the precise physiological cause is not clear (Menser, 1981). It is for this reason that the limited experience gained in spray irrigation of leachate in parts of the United States is not applicable to Ontario conditions. Spraying is routinely carried out in the vegetative dormant months of October to April when direct contact between foliage and leachate can be averted. Leachate spraying is not possible in Ontario during this same period due to the occurrence of air temperatures below 0°C (Gartner Lee Assoc. Ltd., 1984). Thus, some degree of biological and/or physico-chemical pre-treatment of the leachate must be effected to remove the more offending contaminants if this means of treatment is to be successfully adapted to Ontario climatic conditions.

Most research work in this area has focused on comparing the efficiency of various grass species as contaminant concentrating media as well as studying the relative rates of survival with prolonged applications (Menser et al., 1979a). In this respect, forest trees are not as efficient in utilizing leachate constituents as many agricultural crops (Sopper, 1975). In addition, many of these nutrients are redeposited annually as leaf and needle litter, although in less mobile or more benign forms. With regard to mortality, even irrigation with sewage wastewater has been shown to cause a significant decline in the number of tree seedlings and in understory vegetation. Again the exact causes are not evident although the establishment of radically different soil moisture and fertility regimes are no doubt involved. Deciduous tree species and forage grasses have been shown to withstand leachate irrigations of as much as 155 cm over an 8-month period from October to April (Menser et al., 1979b). Observed depression in growth may be related to the low aeration levels in the soil rooting zone induced by high COD leachate application (Menser, 1981).

Methodologies and Preliminary Results

Within the broad objective stated earlier, four more precise areas of investigation provided the terms of reference for the 1986 field season. These were studies of site hydrology and leachate volume reduction, soil quality for leachate disposal, ecosystem stress from leachate irrigation, and physico-chemical pre-treatment of leachate. The ensuing sections provide an inexhaustive outline of the research activities under each heading as well as some preliminary results.

1. Site Hydrology and Leachate Volume Reduction

A major research effort was directed toward identifying means of reducing the total volume of leachate being generated and handled at the Muskoka Lakes site due to the recent expansion of the actual spray area in 1985 and the uncertainty regarding the long-term attenuation capacity of the local glacio-fluvial sands for land disposal.

Of paramount concern was the ability of the existing silty clay to silty clay loam landfill cap to adequately reduce surface infiltration of precipitation. A grid inventory performed of the cap itself indicated that the clay material was both discontinuous and thin (i.e. less than 10 cm) where present. The incomplete sealing of the landfill was in part a consequence of the lack of locally available clay soil for capping material. Saturated hydraulic conductivities (K_{sat}) obtained on intact cores using the constant head method confirmed both the impermeability of the clay material if properly applied to an adequate depth (minimum $K_{sat} = 5.1 \times 10^{-8} cm \cdot s^{-1}$) and its unsuitability for this purpose if mixed with the local sandy soils in thin lifts (maximum $K_{sat} = 5.5 \times 10^{-4} cm \cdot s^{-1}$). Low altitude false-colour infra-red photography confirmed these cap discontinuities through the observation of differential vegetative moisture stress in areas of the grassed landfill with and without the clays of high moisture holding capacity.

A further experiment is ongoing involving possible alternative capping materials. A series of nine 1m x 1m plots were established on the landfill in 1986 to test the ability of various materials or soil treatments situated under a 5 cm layer of turf to reduce or eliminate downward percolation of precipitation once infiltrated. These treatments included the local sand and the existing sic/sicl cap under both compacted and uncompacted conditions, a bentonite slurry with and without sand incorporated, a bentonite-polyvinyl alcohol (PVA) mixture, an industrial polymer-sand mixture, and plastic. By comparing the volume of water applied to each plot when at field capacity to the volume recovered as interflow over the treated soil layer, a simple moisture balance allows for the calculation of the volume lost to deep drainage. Preliminary results indicate that the industrial polymer-sand mixture and the bentonite slurry approach the total exclusion of water that a plastic liner affords while allowing enough deep drainage to promote microbial decomposition of the landfilled refuse (see Table 1). All other treatments fell well short of the optimum degree of impermeability. Of importance is that the industrial polymer is available at no cost making it a much more attractive option than the expensive plastic liners now used at some landfill sites in the United States. A further investigation is now underway to ascertain the long-term weatherability and strength of the polymer-sand mixture in the field, particularly over a winter season.

Table 1. Results of a soil moisture balance for a single irrigation event on the alternative landfill cap plots.

	Soil Moisture Balance for Irrigation Event - Sept. 20, 1986			
Soil Treatment	Depth of Irrigation	- Actual Evapotranspiration	= Runoff Collected	+ Deep Drainage
	mm	mm	mm	mm
Plastic	8.10	2.43	5.67	0
Polymer-sand	8.10	2.43	4.25	1.42
Bentonite slurry	8.10	2.43	4.66	1.01
Bentonite - PVA	8.10	2.43	3.14	2.53
Bentonite - sand	8.10	2.43	2.84	2.83
Existing clay cap	8.10	2.43	1.82	3.85
Compacted clay cap	8.10	2.43	0.81	4.86
Sand (control)	8.10	2.43	2.73	2.94
Compacted sand	8.10	2.43	2.94	2.73

A second research effort in the hydrology area was aimed at reducing the quantity of groundwater in contact with the landfilled refuse. An extensive piezometer network was installed early in the project to determine the major groundwater flow patterns in the vicinity of the landfill. From this it was found that a natural ravine located immediately to the north of the landfill diverts groundwater flow originating from the north toward the perennial stream, thus circumventing any direct contact with the landfill. An exposed bedrock ledge situated upgradient and adjacent to the landfill further diverts any groundwater flow from the east around the landfill. Thus, major groundwater diversion works are not believed to be necessary at this site. Indeed, most of the leachate collected on an annual basis can be accounted for by rainfall amounts directly incident on the landfill area.

In order to test the feasibility of dewatering the area beneath the landfill to eliminate any leachate mounding in the refuse, a 6 m long x 75 cm diameter steel culvert and a number of piezometers were installed at the base of the landfill (see Figure 1). The location for the well was determined with the use of a Geonics EM31 electromagnetic induction meter in an area of apparent concentrated leachate flow. This instrument, by enabling the mapping of concentration isolines, also confirmed the general direction of groundwater flow as being from the landfill to the leachate collection trench. A pump test performed on the culvert well established that the drawdown was significant even after only eight hours of maintaining the well at its minimum level (i.e. 20 cm drop in a piezometer 10 m distant). It is anticipated that continuous pumping from this well would improve the quality of the leachate with time as the groundwater was removed from direct contact with the landfilled refuse.

2. Soil Quality for Leachate Disposal

The present spray area of 4.3 ha is made up of two distinctly different landscape units. Spray areas 1 and 2 (see Figure 1) consist of a shallow veneer (less than 2 m deep) of rapidly permeable fine and medium sands with occasional silty or gravelly substrata. Spray area 3 is comprised of deeper and more homogeneous fine and medium sands (generally greater than 3 m deep) with few textural discontinuities. The recommended design application rates of 2.3×10^4 $\ell \cdot ha^{-1} \cdot day^{-1}$ (April, May, September, October) and 3.4×10^4 $\ell \cdot ha^{-1} \cdot day^{-1}$ (June-August) have been based on a very simplistic water balance with little regard for soil infiltration rates, water storage capacities, attenuation capacities, depth of bedrock, or the composition of the leachate itself. This segment of the study involved the characterization of the local soils and their water regimes both in situ and in the laboratory in order to refine these application rate recommendations.

Table 2 outlines the extent of volatile organic loss from the point that the leachate leaves the vicinity of the landfill in the groundwater flow system (i.e. culvert well sample) to the point when it is ejected from the spray nozzle. Loss of metallic inorganics from the leachate collection trench to the settling lagoons is not as marked, with iron (Fe) decreasing from 49 to 11 $mg \cdot \ell^{-1}$.

Of equal importance to contaminant concentration changes along the collection-disposal system is the distribution of spray around the nozzles and with distance from the pumping station. The overhead spray nozzle type used in this system results by design in an exponential decline in irrigation water depth with distance from the nozzle. This, when combined with the appreciable line pressure drop with distance from the pumping station as well as the frequent malfunctioning of individual nozzles and pump breakdowns in 1986, gave rise to a serious leachate distribution problem over the three spray areas.

Table 2. Loss of volatile organic contaminants along the Muskoka Lakes leachate collection - disposal system.

Volatile* Organic Species	Sampling Location (July 31, 1986)			
	Culvert Well	Leachate Collection Trench	Leachate Settling Lagoons	Spray Nozzle
	$\mu g \cdot \ell^{-1}$	$\mu g \cdot \ell^{-1}$	$\mu g \cdot \ell^{-1}$	$\mu g \cdot \ell^{-1}$
Toluene	1900	2000	106	138
Meta-xylene	100	42	0	6
Ortho-xylene	62	25	8	6
Ethylbenzene	54	23	0	0
Trichloroethylene	18	0	0	0
Benzene	17	8	0	0

* volatile organic analyses performed at the Ontario Ministry of the Environment laboratories.

Soil characterization in the field included a number of detailed soil pit descriptions which revealed the presence of fully developed or developing iron-indurated B horizons ("ortsteins"). Most soils examined belong the Sombric or Dystric Brunisol Great Groups and are in the embryonic stages of the "podzolization" soil-forming process. Large loadings of iron-laden leachate thus accelerate this process leading to major soil morphological changes which can radically alter a soils water and fertility regimes.

The fate of leachate contaminants in the soil was ascertained at three "monitoring stations" with the use of suction lysimeters installed from 15 to 120 cm below the surface. In addition, the soil water regimes of these stations were characterized using a network of tensiometers installed also from 15 to 120 cm below the surface, a neutron thermalization soil moisture depth gauge, and groundwater table observation wells. Field saturated hydraulic conductivity (K_{fs}) was further measured using the Guelph Permeameter method. A mean K_{fs} of 7.5×10^{-3} $cm \cdot s^{-1}$ was obtained in the deep, unirrigated sands near spray area 3 which corresponds to the high conductivity (H1) category of the Agriculture Canada macrostructural description scheme (McKeague et al., 1986). A methylene blue dye infiltration experiment on the forest floor indicated that significant quantities of surface applied leachate can move rapidly to depths beyond the root zone by preferential flow along old root channels. The importance of the forest litter layer in leachate retention and renovation is exemplified by the measured $\psi(\theta)$ soil moisture characteristics for a sandy soil outside of the spray areas (see Figure 2). The LFH/Ah horizon will be in a constant state of flux with irrigation between a near saturated state and the permanent wilting point (θv = 86-39% $m^3 \cdot m^{-3}$) whereas the C horizon will remain closer to a metastable equilibrium between 29% and 9% $m^3 \cdot m^{-3}$.

Soil attenuation capacities are further being evaluated in a leaching column experiment. Intact soil columns (4.5 cm diameter x 75 cm long) were extracted in clear acrylic tubes from both sprayed and unsprayed locations. These columns are being subjected to surface applications of raw leachate as well as lime- and activated carbon-treated leachate at rates of 3, 7 and 14 $mm \cdot day^{-1}$. Soil morphological and chemical changes are being monitored for each treatment as is the quality of the liquid extracted periodically at the base of the columns. The use of sprayed and unsprayed soils will also assist in determining the effect of leachate spraying on long-term soil attenuation capacities.

3. Ecosystem Stress from Leachate Irrigation

The visible damage observed in 1986 and previously in the tree and understory vegetation within the spray areas indicates that the practice of spray irrigating leachate into the hardwood forest ecosystem is effecting major stresses on the biota. At this point in the study, the key stresses are thought to be related to i) the phytotoxicity of leachate in direct contact with plant foliage and roots and, ii) marked changes in the soil moisture and aeration regimes brought about by excessive and inequitable application rates of relatively high COD wastewater (i.e. about 1200 mg $COD \cdot \ell^{-1}$).

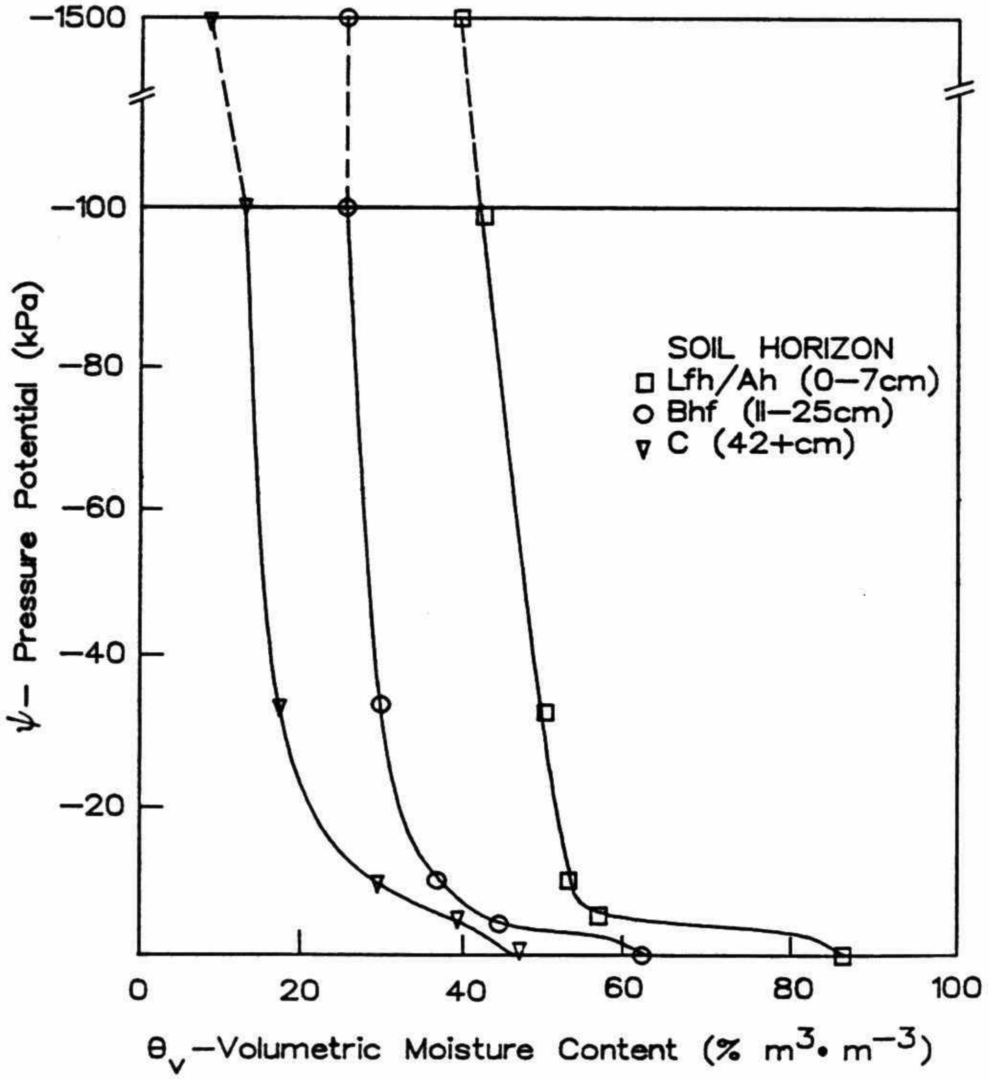


Figure 2. Measured ψ(θ) soil moisture characteristics for three soil horizons from an unsprayed soil.

Vegetative and soil microbial stresses were measured in the field using a number of techniques. Time sequenced, low altitude infra-red photographs demonstrated that vegetation decline and mortality is likely a threshold phenomenon. Spray areas 2 (moderate spray rate) and 3 (light spray rate) showed little visible evidence of stress on the photography while tree canopies in spray area 1, which received a heavy spray loading in the spring of 1986, showed lighter shades of magenta compared to unsprayed trees (Murtha, 1972). Several large gaps in the canopy were clearly visible to the southwest of the leachate lagoons where a more limited spray program was undertaken in the early 1980's.

A total of nine circular, 0.1 ha plots were established in 1986, three in each of a control area (north of the hydro corridor), light spray area 3 and heavy spray area 1 (see Figure 1). Tree growth and productivity measurements in the plots included mid-canopy foliage samples for plant nitrogen determination and stem increment borings for assessment of age and annular ring width using the T.R.I.M. system.

The influence of leachate spraying on forest transpiration and leaf stomatal resistance was measured in the understory and tree mid-canopy with a Li-cor LI-1600 steady state porometer. Some of the results for beech and maple understory vegetation are given in Table 3. Porometer measurements taken on the same day under relatively constant atmospheric conditions for the beech understory show a significant increase in diffusive resistance and decline in transpiration rate with increasing intensity of leachate spraying. A similar trend is evident for maple seedlings even under variable ambient environmental conditions on different sampling dates. This information was complemented by a study of understory community dynamics which sought to relate the presence of certain hydrophilic species (e.g. sedges - Carex spp.) to the transition to wetter soil moisture regimes in the spray areas.

The importance of soil microbial populations to plant nutrient availability and uptake (e.g. mycorrhiza) and to the renovation of leachate in a forest ecosystem prompted a further study of spray irrigation-induced effects on soil microbes. Figure 3 provides the results from a microbial biomass experiment performed in August and October, 1986 on soil cores taken at three depths and in two different spray environments plus a control. The biocidal procedure involves the measurement of the difference in total organic carbon between chloroform-fumigated and non-fumigated soil cores which represents an approximate measure of soil microbial biomass (Jenkinson

Table 3. **Measurements of diffusive resistance and transpiration rates of beech and maple understory vegetation exposed to leachate spraying.**

Understory Species (sampling date)	Treatment	Sample Size (n)	Means (Standard Errors in Brackets)				
			Diffusive Resistance	Transpiration Rate	Photosynthetically-Active Radiation	Relative Humidity	Leaf Temperature
			$s \cdot cm^{-1}$	$\mu g H_2O \cdot cm^{-2} \cdot s^{-1}$	$\mu E \cdot m^{-2} \cdot s^{-1}$	%	°C
Beech							
(Aug.31/86)	Control (non-spray)	29	2.78 (0.075)	4.127 (0.091)	13.5 (1.25)	34.69 (0.037)	21.0 (0.05)
(Aug.31/86)	Moderate Spray	34	3.47 (0.110)	3.422 (0.107)	176.9 (55.47)	34.77 (0.047)	21.3 (0.11)
(Aug.31/86)	Heavy Spray	29	3.69 (0.140)	3.207 (0.117)	21.2 (4.56)	34.54 (0.019)	21.0 (0.02)
Maple							
(Aug.13/86)	Control (non-spray)	95	3.21 (0.094)	3.776 (0.106)	29.9 (4.99)	38.47 (0.50)	22.0 (0.06)
(Aug.18/86)	Moderate Spray	117	5.20 (0.209)	1.557 (0.067)	54.9 (15.74)	63.79 (1.02)	22.6 (0.16)
(Aug.11/86)	Heavy Spray	83	6.94 (0.290)	1.564 (0.069)	219.6 (37.92)	42.01 (0.01)	19.3 (0.05)

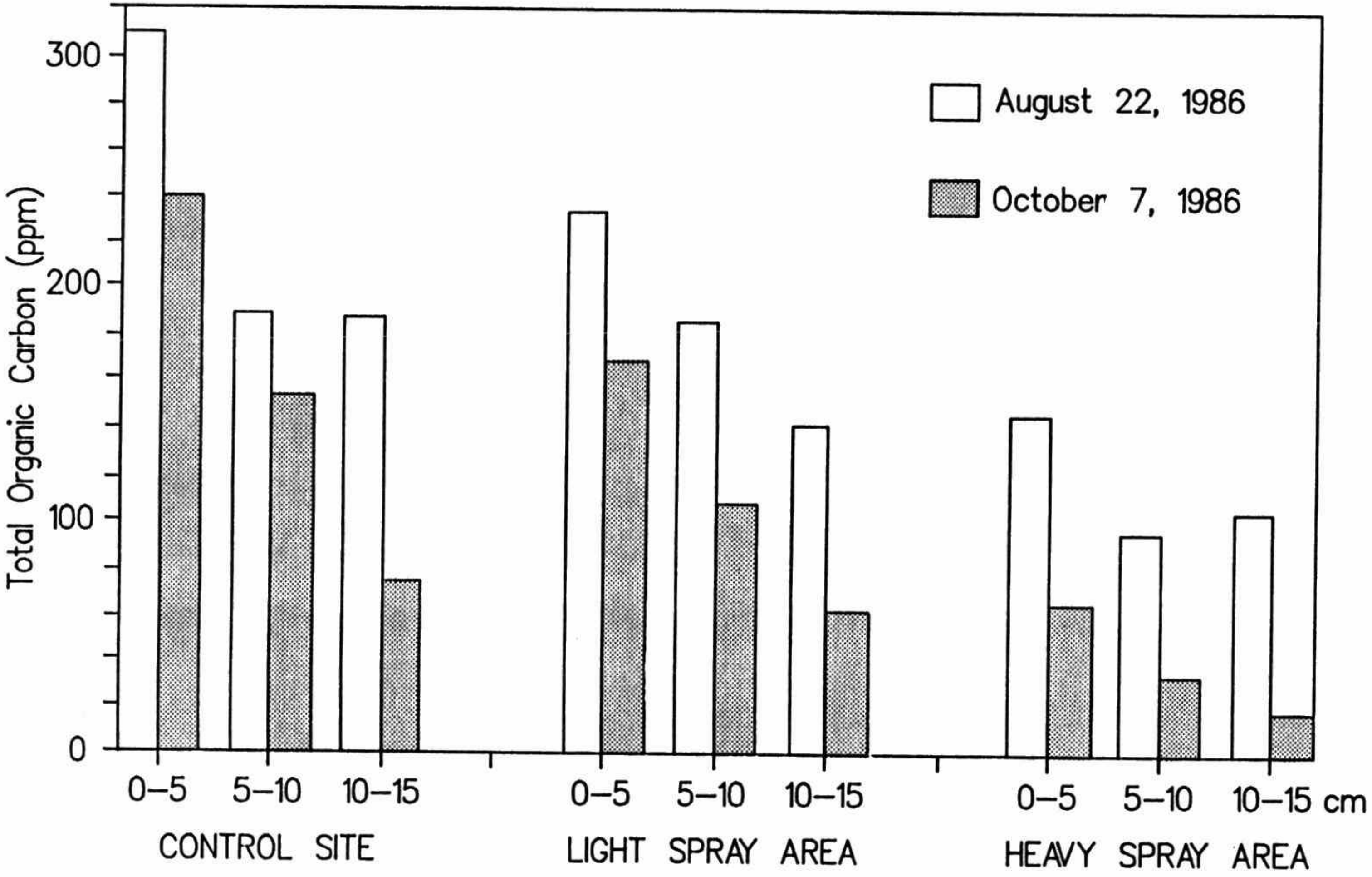


Figure 3. Total organic carbon from soil microbial biomass after biocidal treatment with chloroform.

and Powlson, 1976). Apart from the expected decline in microbial biomass between summer and fall and with depth in the soil, Figure 3 shows a significant decrease in biomass with increasing intensity of spray irrigation at comparable soil depths. A concurrent microbial respiration experiment conducted on the same nine permanent plots, however, did not support the supposition that microbial activity would follow the same trend. A shift in microbial species with wastewater irrigation is presently being investigated as a possible explanation of this inconsistency.

Vegetative and soil microbial stresses are also being investigated in an atmospherically-controlled greenhouse environment. Potted red and sugar maple seedlings have been subjected to a prolonged series of treated and untreated leachate applications to the soil and/or the plant leaves in order to study possible plant physiological changes and partitioning of assimilated contaminants amongst the plant roots, stems, and leaves. Apart from some foliar staining, very few visible symptoms have been observed when leachate is applied at rates sufficient only to meet the atmospheric evapotranspirational demand. Other related ongoing experiments include sugar maple seedling response to soil waterlogging with leachate and soil nitrogen mineralization rate changes with wastewater irrigation.

4. Physico-chemical Pre-treatment of Leachate

A final area of investigation in this study is the determination of an appropriate physico-chemical means of leachate pre-treatment to minimize the adverse effects of spray irrigation on vegetation and soils at the Muskoka Lakes site. A necessary precursor to this study phase is the resolution of the nature of observed phytotoxic effects on vegetation and the scope of soil physical and chemical property changes with prolonged irrigation. Priority pollutant analyses indicate that toluene and Fe are the organic and inorganic constituents of highest concentration, respectively. Both organic and inorganic contaminants can be removed to differing degrees using techniques as varied as high pressure reverse osmosis, upflow sludge bed-filters, downflow stationary fixed-film reactors, activated carbon filtration, aeration, slaked lime addition, and filtration through natural materials such as peat moss or tree bark. Some of these methods can be used together in multi-phase treatment, such as the Environment Canada mobile RO/activated C unit. Lime pre-treatment of leachate to remove metals, however, has proven incompatible with upflow sludge bed-filtration systems which lower effluent COD (Kennedy and Guiot, 1986).

A laboratory pre-treatment study is being conducted which will compare the relative effectiveness of activated carbon (Calgon Filtrasorb 300), $Ca(OH)_2$ (0.25-2.50 $mg \cdot \ell^{-1}$), aeration, and filtration through bark of various tree species in removal of Fe and toluene from leachate samples. Aeration or addition of slaked lime causes the rapid precipitation of ferrous iron and promotes volatilization of many organic compounds. While there are no cation exchange sites in activated carbon for the adsorption of Fe, it has been observed thusfar in this experiment that Fe readily precipitates on the granular carbon surfaces. This, when combined with the broad spectrum removal of organic compounds by the activated carbon, effects a high degree of leachate renovation. Tree bark has been successfully used to remove Fe, Al and Mn from drainage wastewaters through the formation of organic complexes ("chelates") with tannins and phenolic compounds (Vaughan et al. 1984). For example, 1 tonne of dry, weathered pine bark can irreversibly absorb at least 65 kg of elemental Fe from wastewater. Under the present conditions at Muskoka Lakes, this quality of bark would become saturated with Fe after about 18 days assuming a 50 $\ell \cdot min^{-1}$ mean flow rate and 50 $mg \cdot \ell^{-1}$ Fe in the leachate.

Summary

Investigations made of site hydrology suggest that large scale groundwater diversion works are not required at the Muskoka Lakes landfill. The long-term resolution of the leachate generation problem, however, rests on the achievement of both a suitable reduction in landfill cap infiltration and removal of groundwater in contact with the landfilled refuse through site dewatering. With prolonged pumping, the leachate quality should improve with time.

Given the nature of the local soils, the forest floor litter layer is key to increasing the residence time of the wastewater in the unsaturated zone and effecting a suitable level of renovation before the effluent reaches the groundwater table. High water table levels and shallow bedrock over much of spray areas 1 and 2 greatly reduce this residence time and cause the formation of leachate breakouts in depressional areas. The wastewater distribution system is currently less than satisfactory which gives rise to localized application rates far in excess of evapotranspirational demand and soil attenuation capacity. The removal of Fe from the leachate is necessary to avert major soil morphological changes with long-term spray irrigation.

Major transformations in the soil water regime due to heavy leachate loadings and soil morphological changes are responsible for adverse impacts on forest microbial populations, forest understory communities and tree vigour. More specifically, spray irrigation of leachate induces a relatively rapid forest decline caused by a sequence of factors as outlined in Table 4.

With total treatment of leachate (reverse osmosis/activated carbon), it may be possible to discharge the permeate into the perennial stream without the need to spray irrigate. With partial treatment to remove Fe only (tree bark, lime, aeration), spray irrigation could be continued with more aesthetically acceptable results and with less forest decline if a better distribution system were implemented. A combination of total (winter) and partial (summer) treatment would reduce treatment costs and lead to an environmentally acceptable resolution of the leachate disposal problem at Muskoka Lakes.

Table 4. Factors responsible for forest decline at the Muskoka Lakes landfill site.

Predisposing Factors	Inciting Factors	Contributing Factors
- coarse soils shallow to bedrock (deficient water and nutrient availability, inadequate root support)	- micronutrient (Fe, Mn) imbalance - low soil oxygen caused by waterlogging and high COD leachate - formation of indurated Fe horizon of low permeability in soil - reduced photosynthesis and transpiration caused by excess soil water and foliar staining in understory	- insect, disease and microbial infestations (e.g. bark beetle, needle fungi viruses, root-decay fungi)

Literature Cited

Dillon, M.M., Ltd. 1980. Township of Muskoka Lakes Pinelands landfill. 13 pp.

Gartner Lee Associates Ltd. 1984. Soil investigation for proposed leachate spray irrigation system - Pinelands landfill site. Final Report. 20 pp.

Harris, W.F., et al. 1976. Disposal of industrial nitrate effluents by means of forest spray irrigation. Proc. Nat. Conf. on Disposal of Residues on Land.

Jenkinson, D.S. and D.S. Powlson. 1976. The effects of biocidal treatments on metabolism in soil I. Fumigation with chloroform. Soil Biol. Biochem. 8: 167-177.

Kennedy, K.J. and S.R. Guiot. 1986. Anaerobic upflow bed-filter: development and application. Proceedings of Symposium on Anaerobic Fixed-Film Digestion, Toronto, Ontario. p. 15-30.

McKeague, J.A., C. Wang and G.M. Coen. 1986. Describing and interpreting the macrostructure of mineral soils: a preliminary report. Technical Bulletin 1986-2E. L.R.R.I. Contribution No. 84-50. Land Resource Research Institute, Research Branch, Agriculture Canada, Ottawa. 47 pp.

Menser, H.A. 1981. Irrigating with landfill leachate. Biocycle 22: 39-41.

Menser, H.A., et al. 1978. Decontamination of leachate from a sanitary landfill by spray-irrigation of a forested ecosystem. Proc. First Annual Conf. of Applied Research and Practice on Municipal and Industrial Waste.

Menser, H.A., et al. 1979a. The utilization of forage grasses for decontamination of spray-irrigated leachate from a municipal sanitary landfill. Env. Pollution 19: 249-260.

Menser, H.A., et al. 1979b. Spray irrigation: A land disposal practice for decontaminating leachate from sanitary landfill. U.S.D.A. Report ARR-NE-4. West Virginia University.

Murtha, P.A. 1972. A guide to air photo interpretation of forest damage in Canada. Canadian Forestry Service, Publication No. 1292, Ottawa, Ont.

Nordstedt, R.A., et al. 1975. Land disposal of effluent from a sanitary landfill. Water Pollution Control Federation Journal. 47.

Papadopol, C.V. 1984. The renovation of waste water combined with intensive silviculture. Paper presented at the 1984 Winter Meetings of the American Society of Agricultural Engineers, New Orleans, Louisiana.

Richenderfer, J.L., et al. 1975. Spray-irrigation of treated municipal sewage effluent and its effect on chemical properties of forest soils. U.S.D.A. Forest Service General Technical Report NE-17.

Sopper, W.E. 1975. Wastewater recycling on forest lands. Proc. Fourth North American Forest Soils Conference, Laval University, Quebec.

Totten, Sims, Hubicki Associates Ltd. 1983. Township of Muskoka Lakes leachate treatment study for Pinelands landfill site.

Vaughan, D., R.E. Wheatley and B.G. Ord. 1984. Removal of ferrous iron from field drainage waters by conifer bark. J. Soil Science 35: 149-153.

CODISPOSAL OF INDUSTRIAL AND MUNICIPAL WASTES. PART II

D.W.KIRK, M.LAU and S.PIRANI

Department of Chemical Engineering
University of Toronto

Key words: Industrial Solid Waste, Municipal Waste Landfill, Codisposal, Leachate.

This work is part of a longer term study of factors involved in the mobilization of metal species from solids contained in a landfill environment. Current methods of testing for the suitability of solids for disposal in municipal landfill sites do not take into account the anaerobic environment generated by microbial action or the role of biological metal mobilization, and thus the screening tests may not provide the appropriate information required.

In an earlier report the standard EP leach test for a steel flue gas dust was compared with modified leach tests with mixed municipal refuse and the steel flue gas dust. In this report , results from experimental landfill test columns are presented. The columns are designed to provide data on metal mobilization within a municipal refuse landfill with and without various loadings of the steel flue gas dust. Both atmospheric and controlled water input are compared.

The results of the work show that the presence of the industrial waste has a beneficial effect in inhibiting the release of many metal species over the timeframe studied.

Introduction

The disposal of solid wastes has traditionally been carried out by landfill methods because of public acceptance and economics. Despite the long history of this technique, little is known of the complex interactions that take place within a landfill site. Thus the classification of solid wastes into those suitable for disposal with municipal solid wastes and those considered hazardous and therefore requiring disposal with industrial wastes in secure landfill sites, is not based on the behaviour of the waste in the landfill environment, but rather on laboratory screening tests. With growing public concern over all types of disposal sites, it is important to review the screening tests and to correlate the data with observed behaviour. It is in this context that the present work is given.

The study currently in progress has a much broader scope to investigate and model the factors involved in metal mobilization within the environment of a municipal solid waste landfill. This investigation will permit the rationalization of criteria for solid waste disposal and ultimately allow better landfill practices.

The most widely accepted screening tests for determining the suitability of solids for disposal with municipal refuse are the U.S. Environmental Protection Agency's EP test, and the Ontario Ministry of the Environment's LEP test. Both utilize a 24 hour leaching period with acetic acid added as a buffering agent. The conditions of liquid to solid ratio, temperature, amount of acid, and type and rate of tumbling action are set so that reproducible measurements can be obtained. As a result of the time frame of the test, it is unlikely that conditions representing a landfill environment are properly considered. In particular, the factors that clearly are not included are:

- the anaerobic nature of the landfill
- the metal complexation by microbial action and organic species
- the attenuation processes occuring in the municipal refuse
- the effect of the waste on the microbial population of the municipal refuse environment
- the pH buffering capacity of the leachate generated within the landfill

It should be pointed out, however, that the significance of these various factors has not been established, so that the limitations of the screening tests cannot be accurately gauged. In order to evaluate these factors, a two part experimental program was begun.

In the first part, the leaching behaviour of a steel flue gas dust was studied using the LEP method and several variations. This work was reported previously (1). In the second part, leaching columns (193 cm x 33 cm diameter) were set up for measurements of leachate quality of municipal waste with and without industrial waste (the flue gas dust). Thus a comparison of the leach test results can be made with the simulated landfill measurements. The column measurements representing the simulated landfill conditions were run with both atmospheric conditions and intermittent controlled water additions. Four compositions were tested: municipal solid waste (MSW), municipal solid waste with 8% industrial waste (by weight) (MSW + 8% IW), municipal solid waste with 30% industrial waste (MSW + 30% IW), and 8% industrial waste in sand (8% IW + sand). The industrial waste used was from the same batch of steel flue gas dust and was layered rather than dispersed in the municipal waste.

Methodology

Short Term Laboratory Leach Tests

1. LEP Tests

The extraction procedure used in this work followed the LEP method with the proportions reduced to treat 50g of solid rather than the 100g usually employed. In brief, the technique consists of adding 50g (dry weight) of solid to a 1250mL polyethylene bottle with 800mL of deionized water. The pH is adjusted with acetic acid to pH 5.0, provided that the addition not exceed 4 mL of 0.5M acetic acid per gram of sample. The polyethylene bottle is placed on a rotary extractor for a 24 hr period. The solution is then made up to the 1000mL amount to give a 20:1 liquid to solid ratio. The resulting solution is analyzed using standard procedures. The details of the procedure may be obtained from the Ontario Ministry of the Environment.

2. One Month Leach Tests

Solid samples of 50g consisting of municipal solid waste (MSW) and MSW + 8% industrial waste (IW) were treated with the same 20:1 solution to solid ratio using the acetic acid solution described above and deionized water. In these tests, polyethylene bags were used and were hand agitated on a daily basis. Analyses were conducted in an identical manner to the LEP tests.

Long Term Column Tests

A schematic of the columns used is shown in Figure 1. The details have been previously described (1). Four different column compositions were tested: MSW, MSW + 8% IW, MSW + 30% IW and 8% IW + sand. One column for each composition was left open to the atmosphere to receive natural precipitation, and one column for each composition was closed to receive regular water additions, according to an 11 year average monthly rainfall. Each of these columns was run in duplicate giving a total of 16 columns. The columns were insulated and heated in the winter period to avoid freezing. The leachate which collected at the base of the columns was pumped out on a weekly basis to simulate the unsaturated flow found in landfill sites, and samples were taken and analyzed.

Analysis

Samples were analyzed by both ICP (inductively coupled plasma) spectroscopy, and NAA (neutron activation analysis). A total of

18 elements could be analyzed by ICP, though only 12 were measured on a routine basis: Mg, Al, Mn, Cu, Ca, Fe, S, Pb, Zn, Cd, Ni, and Cr. NAA was used routinely for 9 elements: Mg, Al, Mn, Cu, Ca, Br, Na, K, and Cl. The element overlap for the two analytical techniques allowed for cross checking. In addition, NBS standards were used to calibrate the methods. In general, excellent agreement was found for the two methods.

Municipal Solid Waste

The municipal solid waste (MSW) used in this study was collected in the Metropolitan Toronto area. A blend of summer and fall samples was used. The compositon, shown in Table 1, was provided by the Ontario Centre for Resource Recovery. The MSW was shredded for uniformity, and a screen size analysis is shown in Table 2. The metal content of the MSW by ICP and NAA is shown in Table 3.

Industrial Waste

The industrial waste used in this study was collected from a steel producer in Ontario. A chemical analysis of the IW is shown in Table 4. A particle size distribution of the IW is shown in Table 5.

Results

Short Term Tests

The LEP test results for MSW, MSW + 8% IW and IW are shown in Table 6. It is clear from the results that the industrial waste would not pass the screening test, based on the amount of lead solubilized. This is a consequence of the alkaline nature of the IW and the limit set for acid addition in the test. The steel flue gas dust has sufficient sodium, potassium and calcium oxides (or hydroxides) to maintain an alkaline condition after 0.1 moles of acetic acid have been added. The consequence is that the solubilities of certain metals (Mg, Al, Mn, Cu, Fe, Zn, and Cd) are suppressed. This is especially obvious from the fact that all these elements are more concentrated from the 8% IW sample. The elevated concentration of lead is due to the biplumbite ion which is soluble in alkaline conditions.

The leach test using MSW + 8% IW shows values that appear to be more realistic, that is, the presence of the IW has increased the concentration of most species. In this test, the maximum levels for lead (5.0 ppm), cadmium (0.5 ppm) and manganese (5.0 ppm) are exceeded, though only by minor amounts (3.7 ppm, 0.23 ppm and 8.3 ppm respectively). The results of the MSW + 8% IW test conducted for a one month period using the static bag technique also are shown in Table 6. In this case there was sufficient time to develop biological action. This has resulted in an enhancement of some metal concentrations such as Mn and Fe, and now has elevated these above desired levels.

Thus from the standard LEP test, the IW would be considered to pose a hazard, but this is the result of the very alkaline nature of the industrial waste. The combination of IW with MSW in the 24 hr LEP test shows that the alkalinity will be reduced, and that lead levels would be close to the maximum target values. However, comparison of the 24 hr LEP test for MSW and MSW + 8% IW shows that the presence of IW increases the concentration of all elements measured, with Cd, Mn, and Pb now exceeding target values. The one month test, allowing microbial action to take place, shows additional solubilization of Mn and Fe above target values.

Column Studies

A plot of leachate generation for the columns packed with MSW, shown in Figure 2, is typical of the variability found for the leachate production. Despite the greater than average precipitation input to the columns, the leachate volume generation is very similar to the controlled moisture columns, thus showing the effect of evaporation on the atmospheric columns. One approach to providing a common basis for comparison of leachate concentrations is to plot the column data as a function of cumulative leachate volume. This method is attractive for this work because the loss of metal ions from the packed columns is likely to be directly related to the flow of water through the column. Until field capacity is reached for a column, the volume of leachate generated is sporadic, so that column data is shown starting at field capacity. The amount of dry MSW averaged 42.6 kg per column.

A plot of the pH of the leachate as a function of time is shown in Figure 3. As can be seen in the figure, the sand columns have maintained very alkaline leachates over the 300 days past the attainment of field capacity. Three of the MSW columns have leachates with pH values about 5.5, while the fourth MSW column has a leachate with a pH value of about 7.0. The MSW + 8% IW and the MSW + 30% IW columns have leachates which fall between these levels. Thus the presence ofIW in the MSW columns does not appear to modify unduly the pH of the generated leachate. Although the elevation of the leachate pH has been reported, the values in this work appear to be within the range of normal variability. A longer time frame may be required to establish the effect of this IW on leachate pH.

The concentrations of most elements in the leachates were found to decrease with cumulative volume increase. In order to provide a comparison of the effect of codisposed industrial waste, the concentrations of metal ions in the first 30L of leachate were compared. This volume represents about 120 days past the attainment of field capacity and is the period of maximum metal ion concentration. The average and maximum concentrations for 14 elements are shown in Table 7, for the MSW, MSW + 8% IW, MSW + 30% IW and 8% IW + sand columns. It is interesting to note that the maximum concentrations recorded for any of the 4 columns in each set ranged from 2 to 5 times the average value for most elements. The comparison between the column sets show that the presence of IW in the MSW does not increase the amount of metal ion in the leachate with a few exceptions. This is most readily seen by calculating the ratio of element concentration in the leachate to the element concentration found in the MSW leachate. These values are shown in Table 8.

Thus, from the column studies, it appears that there is a synergistic effect between the MSW and IW, which improves the leachate quality for most elements. The problem of high lead contamination predicted by the leach tests does not appear, except for the unbuffered sand columns. Lead levels were somewhat elevated for the column tests, from 1.5 to 4.6 times that of the MSW. The previous indications from the one month test, that iron, manganese and cadmium would be elevated by the presence of MSW and microbial action, was not borne out in the column measurements over the time frame studied. Indeed, the concentrations of these elements were suppressed in the MSW + 8% IW leachate. It is not known whether the beneficial action of the IW in the MSW is a long term effect, or whether once the alkalinity has been neutralized, the concentrations will begin to increase.

Conclusions

The screening tests used for determining the suitability of solid wastes for disposal with municipal waste do not appear to adequately account for the buffering capacity of the MSW environment.

Short term (24 hr, 1 month) tests over-predicted the leachability of the IW, or under-predicted the capacity of the MSW for binding contaminants. There was, in fact, an overall improvement of leachate quality with industrial waste codisposed. This effect may be linked to the alkaline nature of the IW, but longer term studies will be required to test whether this effect will persist. A control strategy for limiting the initially high levels of contaminants in landfill leachates , which is suggested by the results, is to use a lime layer in the landfill site.

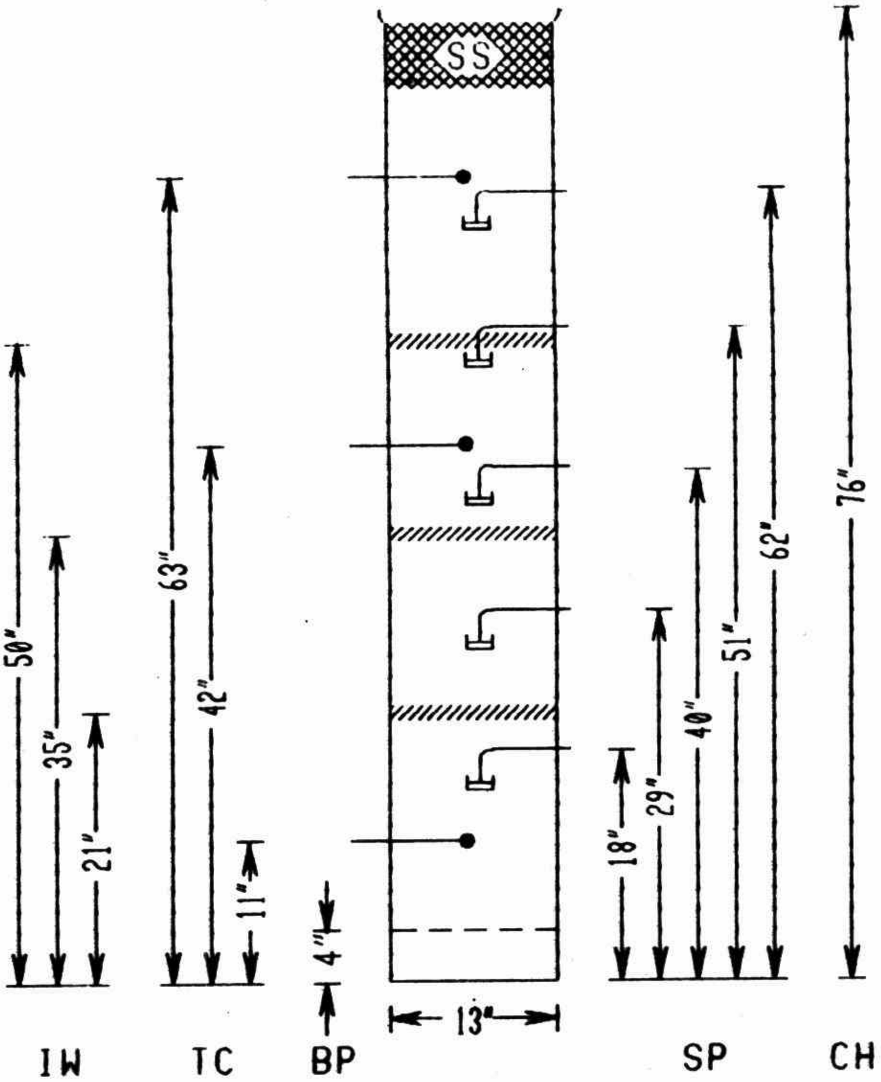
From the results of the tests to date, codisposal of some solid industrial wastes appears to be very attractive.

Acknowledgements

The authors gratefully acknowledge the financial and technical support provided by the Ontario Ministry of the Environment for this project. Also, the authors would like to thank Dr Sheldon Landsberger at the McMaster Reactor, McMaster University, Hamilton for his technical expertise and assistance with NAA analyses.

References

Kirk,D.W. and Lau M. Proceedings: Technology Transfer Conference No.6, Part 3 Liquid and Solid Waste Research. 1985 pp209-243 ISSN0-825-491



Legend :		
	IW	**Industrial Waste**
	TC	**Thermocouples**
	BP	**Bottom Plate**
	SP	**Sampling Ports**
	CH	**Column Height**
	SS	Silica Sand

FIGURE 1 Column dimensions and interior

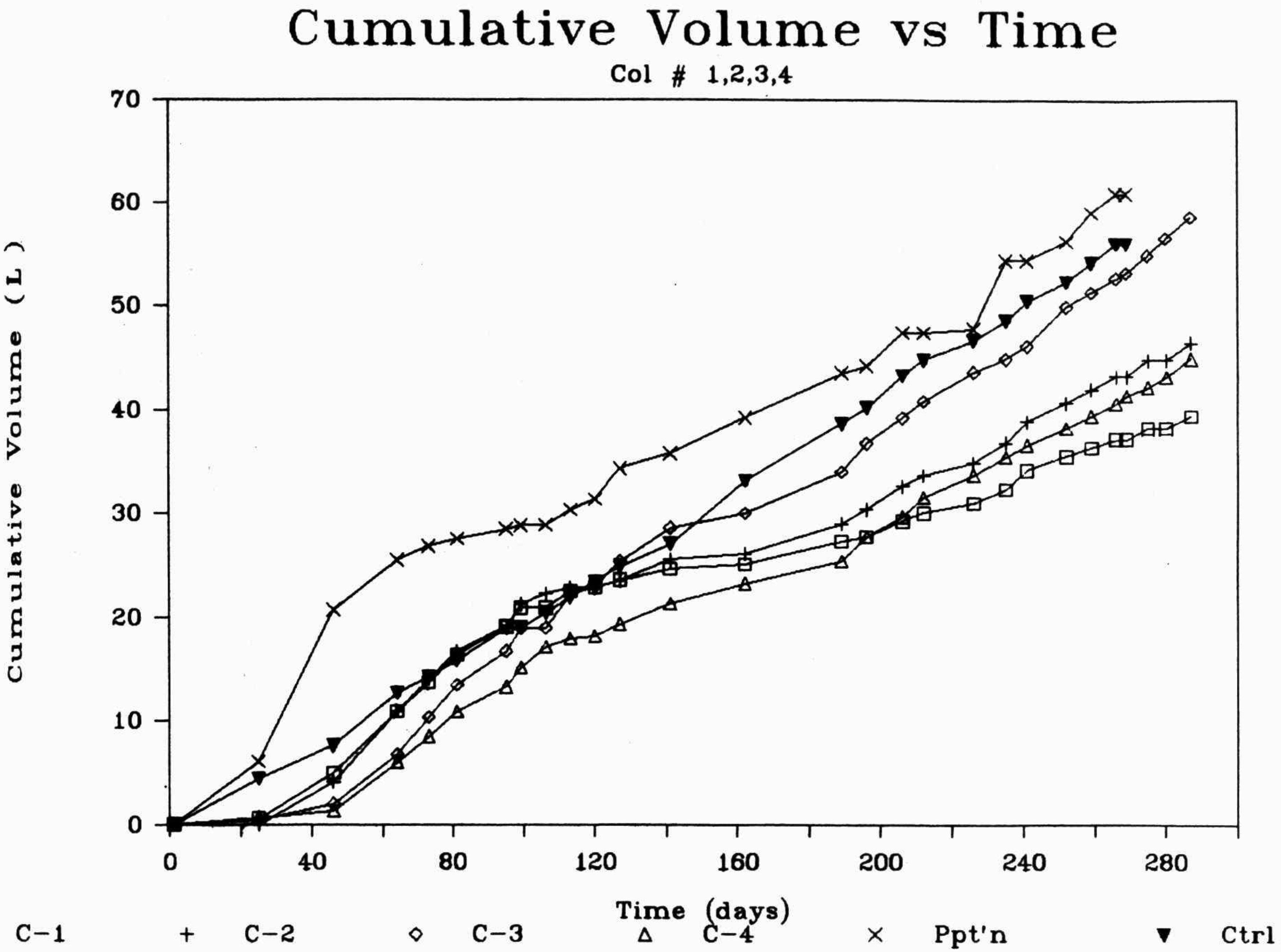

Cumulative Volume vs Time
Col # 1,2,3,4
Cumulative Volume (L)
0
10
20
30
40
50
60
70
0
40
80
120
160
200
240
280
Time (days)
□ C-1
+ C-2
◇ C-3
△ C-4
× Ppt'n
▼ Ctrl

FIGURE 2

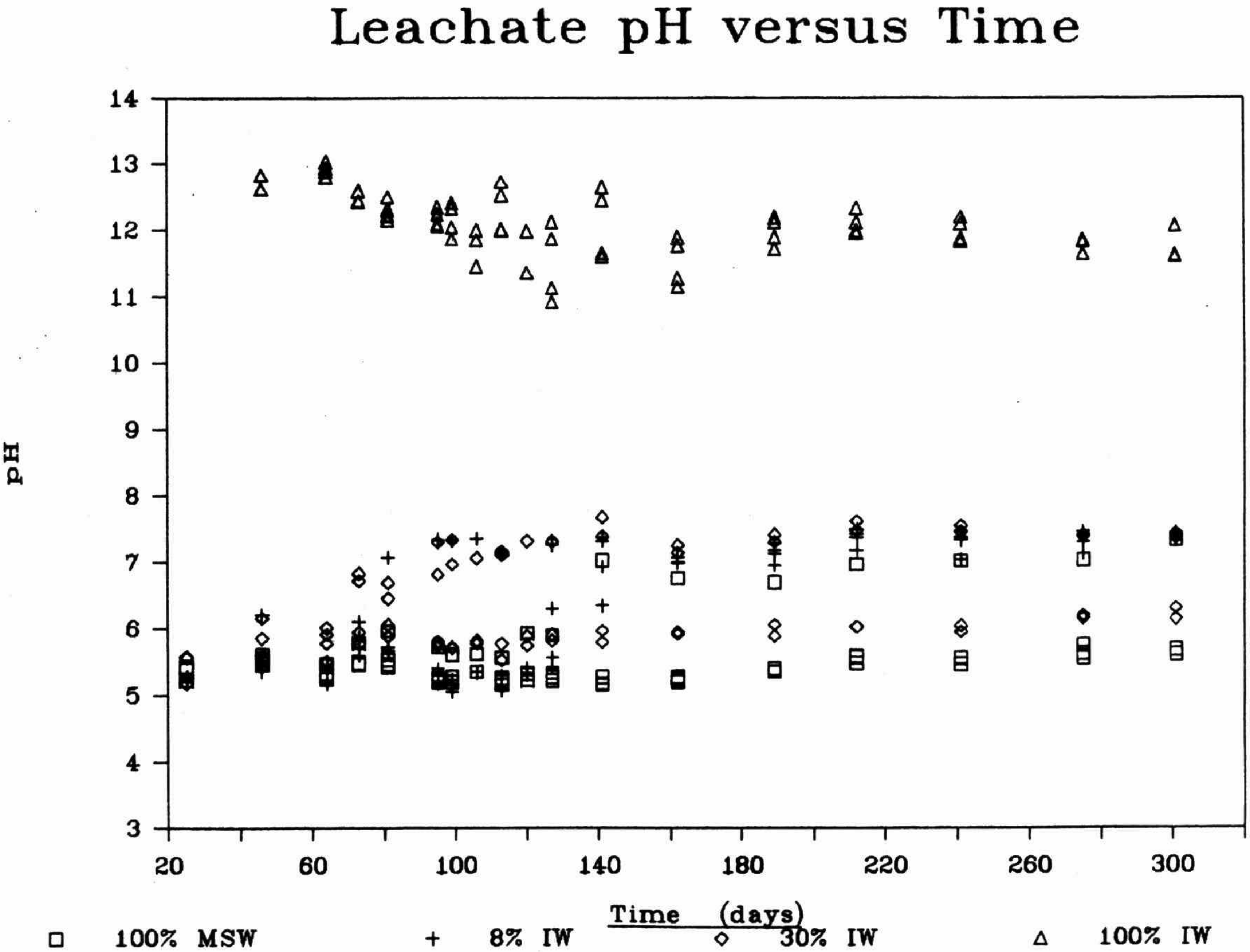

Leachate pH versus Time
pH
14
13
12
11
10
9
8
7
6
5
4
3
20
60
100
140
180
220
260
300
Time (days)
□ 100% MSW
+ 8% IW
◇ 30% IW
△ 100% IW

FIGURE 3

TABLE 1

Municipal Solid Waste Composition (by weight)

	Fall Sample (%)	Summer Sample (%)
ash	45 +/- 4	
moisture	27.2	14.0
Component Analysis		
paper	54.0	25.3
natural organic	0.8	17.0
synthetic organic	7.2	20.4
ferrous material	10.1	8.6
nonferrous material	1.5	-
glass	1.2	1.5
fines	24.9	26.5
TOTAL	99.7	99.3

TABLE 2

Size Distribution of MSW After Shredding

Screen Size	% Retained
+4 inch	0.4
+2 inch	4.0
+1 inch	23.8
+1/2 inch	25.6
+1/4 inch	20.4
+8 mesh	14.9
-8 mesh	10.6
TOTAL	99.7

TABLE 3

Metal Content of the MSW by ICP and NAA

Element	Concentration (by weight)
Mg	980 ± 270 ppm
Cu	120 ± 30 ppm
Na	1.06 ± 0.45%
V	8.7 ± 1.6 ppm
Al	1.84 ± 0.04%
Mn	620 ± 20 ppm
Ca	5.1 ± 0.6%
Cr	88 ± 5 ppm
Fe	3.0 ± 0.4 ppm
Zn	680 ± 5 ppm
Co	18 ± 1 ppm
Cl	750 ± 990 ppm
Ni	25 ± 20 ppm
Cd	7.1 ± 0.2 ppm
Pb	90 ± 20 ppm
S	0.64 ± 0.02 ppm
As	40 ± 2ppm
B	142 ± 6 ppm
Ba	270 ± 30ppm

TABLE 4

Metal Content of the IW by ICP and NAA

Element	Concentration (by weight)
Mg	1.51 ± 0.01%
Cu	0.18 ± 0.01%
Na	0.75 ± 0.08%
V	110 ± 10 ppm
Al	0.205 ± 0.004%
Mn	4.0 ± 0.1%
Fe	27.2 ± 0.5%
Zn	14.1 ± 0.3%
Co	16.1 ± 0.8 ppm
Cl	1.34 ± 0.14%
Ni	410 ± 70 ppm
Pb	1.99 ± 0.002%
Cd	323 ± 9 ppm
S	0.36 ± 0.2%
As	90 ± 10 ppm
Mo	46 ± 10 ppm

TABLE 5

Particle Size Distribution of IW

Mesh Screen Size	Cumulative % (by weight)
+80	16.8
+100	20.0
+140	25.5
+200	30.2
+325	36.5
-325	63.5

+ retained - passed through

TABLE 6

LEP Tests (ppm)

	24 Hour Test				1 Month Test
Element	MSW	MSW + 8% IW	IW	Allowable Limits	MSW + 8% IW
Mg	35.3	50	0.44		50.4
Al	1.8	2.3	0.30	<10>	2.01
Mn	3.3	8.3	0.04	<5>	14.4
Cu	0.25	0.63	0.26	<100>	0.40
Ca	390	812	3956	<8000>	373
Fe	3.69	8.32	0.07	<30>	54.1
S	73.8	78.2	85.9		89.0
Pb	-	8.7	175	5.0	9.26
Zn	3.42	254	6.36	<500>	245
Br	0.28	2.40	24.6		2.47
Na	102	112	260	<2000>	128
K	69.5	74.5	232		102
Cl	105	152	720	<25000>	155
Cd	0.05	0.73	-	0.5	0.54
Cr	0.04	0.14	0.45	5.0	0.13
pH	5.8	5.3	11.9		5.2

< > refers to 100X maximum desirable concentration

TABLE 7

COLUMN LEACHATE COMPOSITIONS (ppm)

Element	MSW		MSW + 8%IW		MSW + 30%IW		8%IW + Sand	
	Avg*	Max	Avg*	Max	Avg*	Max	Avg*	Max
Mg	476	858	343	616	358	606	1.04	2.88
Al	6.42	54.3	9.77	30.0	1.65	7.78	2.92	6.22
Mn	50.7	92.9	25.0	60.3	35.2	68.1	0.12	0.03
Cu	0.46	0.89	0.28	0.73	0.48	1.53	0.15	0.37
Ca	2563	4297	1638	3332	1716	3668	363	1922
Fe	813	1095	450	1170	545	1821	0.1	0.52
S	412	690	149	470	411	725	39	258
Pb	0.64	1.40	2.93	22.0	0.94	2.89	109	589
Zn	51.7	113	20.4	54.8	43.5	107	0.69	3.05
Cd	0.48	4.05	0.08	0.18	0.16	0.31	0.02	0.08
Cr	0.39	1.98	0.32	1.55	0.18	0.49	0.25	0.57
As	0.41	0.53	0.16	0.41	0.42	0.57	0.02	0.05
Co	0.29	0.55	0.18	0.50	0.38	1.50	0.03	0.15
Ni	1.45	2.18	0.93	1.90	0.89	2.41	0.06	0.27

* Average of four columns (2 atmospheric + 2 control)

TABLE 8

Leachate Concentration Enhancement versus MSW Leachate

Element	MSW + 8%IW MSW	MSW + 30%IW MSW	8%IW + Sand MSW
Mg	0.72	0.75	0.002
Al	1.52	0.26	0.46
Mn	0.49	0.69	0.001
Cu	0.60	1.05	0.33
Ca	0.64	0.67	0.14
Fe	0.55	0.67	0.001
S	0.36	1.00	0.1
Pb	4.59	1.47	171
Zn	0.39	0.84	0.013
Cd	0.17	0.33	0.034
Cr	0.80	0.47	0.65
As	0.39	1.04	0.059
Co	0.60	1.28	0.09
Ni	0.64	0.62	0.039

HAZARDOUS ORGANIC CHEMICAL IN GROUNDWATER AT ONTARIO LANDFILLS

James F. Barker
John A. Cherry
Institute for Groundwater Research
Department of Earth Science
University of Waterloo
Waterloo, Ontario N2L 3G1

ABSTRACT

Studies have been conducted at seven landfills in Ontario ranging in latitude from the North Bay landfill in the north to a landfill near Sarnia in the south. The sites represent a variety of geologic materials in which migration of leachate-derived contaminants occurs, including sand aquifers, sandy silty glacial till, clayey glacial till and fractured carbonate/shale. With the exception of the clayey till site, extensive lateral migration (> 200 m < 1000 m) of organic contaminants, particularly the common volatile organics, has taken place. These landfills range in age from one to three decades. The total dissolved organic carbon in the contaminated groundwater is generally in the range of 10 to 200 mg/L. The total load of identifiable organic compounds is only a small fraction of this total. The nature of the suite of characteristic volatile organics differs considerably from landfill to landfill, and to some degree reflects the nature of the industrial base of

the municipality. The spatial distribution of volatile organics within each plume is generally more complex than the distribution of the standard plume indicator parameters such as total dissolved solids, electrical conductance, total dissolved organic carbon and chloride. The design of effective monitoring networks for trace organic contaminants is therefore more difficult.

At the landfill on clayey glacial till, the downward migration of Cl^- and volatile organic compounds was determined through work done in collaboration with the Oregon Graduate Center. Vertical cores were collected from the bottom of a five year old hazardous waste-disposal pit in unweathered clayey material. These cores show that downward contaminant migration has occurred due to molecular diffusion without significant influence of groundwater flow. Chloride has diffused 85 cm in 5 years. Volatile organic compounds have moved at a slower rate due to adsorption. The clayey till below the pit site is 26 m thick and therefore the aquifer below is not threatened. In a different context, however, molecular diffusion is a process that will cause contaminants to move through compacted clay liners relatively quickly even if the liners achieve a very low permeability.

INTRODUCTION

It has long been recognized that municipal landfills in Ontario and elsewhere produce leachate that causes contamination of groundwater. Zones of contaminated water, termed leachate plumes, can be quite extensive at landfills situated on permeable geological materials. Since 1976 researchers at the Institute for Groundwater Research have investigated the physical and chemical controls of contaminant migration at such landfill sites. Since 1982 additional emphasis has been placed on the migration of organic contaminants. Some of these organic studies were conducted in collaboration with researchers from the Environmental Engineering Group at Stanford University and from the Department of Environmental Chemistry and Biology at the Oregon Graduate Center.

Seven landfill sites are currently being investigated. Three sites (Borden, Woolwich, North Bay) are situated on unconfined sand aquifers, one site (new Borden) on unconfined sand and clay tills, one site (Tricil near Sarnia) on clayey glacial till, and two sites (Bayview and Hamilton) on fractured sedimentary bedrock. Thus, a wide range of hydrogeological conditions are included in these studies.

Methods of investigation at all but the Tricil site are summarized by Barker et al. (1984). Essentially, an extensive network of multilevel groundwater sampling devices, termed multilevel piezometers, are established to provide a detailed, three-dimensional picture of contaminant distributions. Hydraulic information obtained by water-level measurement, well-testing, and detailed core analysis defines the groundwater flow system responsible for contaminant migration. Hydraulic testing, piezometer sampling , and laboratory studies of sorption and biotransformation can then be integrated, with the assistance of mathematical simulation when appropriate, to describe the migration of organic contaminants in the plumes.

With respect to organic contaminants, these studies are addressing several questions:

1) what organics are present in landfill leachates?
2) how fast do they migrate in groundwater?
3) how far and for how long do they persist? and
4) what are the processes controlling their migration and persistence?

The fourth question is important to address if the results of these field studies are to be generalized for application to other landfill or waste disposal situations. Only a thorough understanding of the processes will establish a reliable predictive capability.

It is important to study real landfill situations where the results of complex, interactive transport processes are fully apparent. This complexity, however, also limits our ability to identify the contribution of specific processes, such as sorption, dispersion, and transformation, to organic contaminant migration and persistence. The major field limitations are the undefined history of inputs from the waste to the groundwater and the uncertainties in the flow system hydraulics. Laboratory studies, under conditions representative of field sites, are often more useful to evaluate specific processes. Another approach currently being emphasized at IGR is to conduct field-scale experiments in which solute-spiked groundwater is injected into a well-characterized aquifer and the migration of solutes under natural flow conditions is monitored by sampling from a dense, three-dimensional network of multilevel piezometers. This provides for a well-defined input and a well-characterized flow system in which the processes can be more clearly investigated. "Natural gradient injection" experiments were used by Sudicky et al. (1983) to study dispersion of chloride, by MacKay et al.

(1983) for selected halogenated organics, by Sutton and Barker (1985) for selected soluble organics, and by Patrick and Barker (1983) for monoaromatic hydrocarbons. Thus, laboratory and field-scale experiments augment the current studies of organic contaminant migration at landfill sites, all with the aim to better understand the processes controlling organic contaminant behaviour in groundwater.

Barker et al. (1985) described some of the current studies at four of the landfill sites, and Barker (in press) expanded the discussion to include six sites. A detailed characterization of landfill leachate was conducted and specific organics were selected for more detailed study. To date, these studies have emphasized commonly encountered, more-mobile organics which can routinely and reliably be determined in numbers sufficient to provide accurate "snapshots" of their distribution in groundwaters. Studies to date have emphasized two classes of volatile organic contaminants:

1) halogenated, one-and-two carbon hydrocarbons which are common industrial chemicals that regularly occur in household products, and
2) aromatic hydrocarbons, occasionally chlorinated, that are common in petroleum products and other industrial chemicals as well as in household products.

Distributions are then interpreted in terms of the hydrogeological processes (advection, dispersion) and geochemical processes (sorption, chemical and microbial reaction) which must control the distributions.

Some results from the 1984 and 1985 field studies at the North Bay landfill will be presented in this paper. Preliminary results from the

Tricil site, located in thick clayey deposits will also be discussed. In the North Bay site, advection is rapid. In the Tricil site, slow diffusion is the dominant process causing transport of organic contaminants.

THE NORTH BAY LANDFILL LEACHATE PLUME

The most intensively studied landfill site is at North Bay, Ontario (Reinhard et al., 1984; Barker et al., 1986). The landfill lies in a complex deposit of bedded glaciofluvial sands underlain by gneissic bedrock. The site has operated since 1962 and leachate-contaminated groundwater has been observed discharging near a creek, about eight hundred meters from the landfill, since our studies began in 1980. Thus, at this site we have not been able to discuss a plume front, as is found at the other sites. Mobile contaminants have reached the discharge zone, albeit at very low concentrations. This study, therefore, cannot deal with relative velocities of contaminants, but rather provides field evidence of contaminant transformation and persistence during transport in anoxic groundwater.

The organic geochemistry of the leachate is presented by Reinhard et al. (1984), Barker (in press), Barker et al., (1985) and Barker et al. (1986). Figure 1 shows the plan view of the leachate plume and the location of piezometers used to construct cross-sections (Figure 2). Tables 1 and 2 presents the geochemistry of groundwaters along the plume for 1983-1984. Figure 2 shows the distribution of the indicator parameter chloride (Cl) and selected aromatic hydrocarbons in the vertical cross-section along the centre of the leachate plume. Volatile halocarbons do not persist throughout this plume, probably due to their biotransformation under the methanogenic conditions of this plume. Volatile aromatics are more persistent, however, and are found occasionally in the discharge zone, although at significant attenuation. Considerable dilution due to dispersion is evident in the declining concentrations of rather unreactive constituents such as Cl, Na, K, Ca and Mg.

Recent hydrogeological studies (M. Moore, 1986 and N. Gensky, M.Sc. thesis in progress) have identified a relatively thick sand of rather uniform appearance and hydraulic conductivity (about 1×10^{-2} cm s^{-1}) probably extending throughout the flow system. Average groundwater velocities appear to be from 4×10^{-4} cm s^{-1} to 1×10^{-3} cm s^{-1}. Unretarded contaminants could, therefore, be moving through the flow system within two to four years.

Spatial and temporal variability of contaminant distributions have been the focus of recent studies (Barker et al., 1985). The general shape of the leachate plume has not changed since about 1980 although there has been considerable fluctuation in the concentration of the indicator parameters chloride (Cl) and dissolved or total organic carbon (DOC of TOC). The general distribution of organic contaminants is similar (Figure 2). Sampling during 1985 on a monthly basis revealed considerable temporal variation in the indicator parameters and aromatic hydrocarbons (Figure 3). This variability may be seasonal, but further data assessment is required to evaluate the seasonality.

There appears to be only a poor correlation between the indicator parameter Cl and the organic contaminant benzene at piezometer G-5 (Figure 3). To evaluate the correlation between indicator and trace organic parameters, a series of simple statistical tests were performed. All the pairs of chloride plus benzene, chlorobenzene, and 1,2,4-trimethylbenzene for groundwaters sampled in 1985 from the multilevel piezometers G, LL and AAA were used. Linear regression equations were developed for the chloride-organic pairs and the linear correlation coefficients calculated. The results are shown in Table 3. Near the landfill at piezometer G, there is essentially no correlation of chloride with the trace organics. This suggests that the leachate input is rather irregular and that the landfill is not a constant source of these contaminants. Further along the flow system at piezometer LL, the contaminants benzene and chlorobenzene show a much better correlation with the indicator parameter. At LL, the 1,2,4-trimethylbenzene concentrations were often below the analytical detection limit (about 0.2 ug/L) and so no correlation was attempted. This improved correlation at lL is intriguing. Could it be that the processes controlling contaminant transport, particularly dispersion, sorption and biodegradation, are acting to smooth the erratic Cl-organic relationship observed near the landfill? This aspect is under investigation (Gensky, M.Sc. thesis, in progress). In the discharge zone the organic concentrations have dropped considerably so that most samples contained only undetectable levels of organics, except for benzene. The Cl-benzene correlation was established by assigning the undetectable benzene concentrations as the detection limit (0.2 ug/L). The resulting correlation is very poor, in part due to this assignment. However, it does appear that the aromatic hydrocarbons are being biodegraded as well. This process probably contributes to the lack of Cl-benzene correlation; biotransformation removes benzene even from high-Cl samples, leaving variable Cl concentrations in samples, with low and less-variable benzene concentrations.

Because of time and financial constraints, leachate plumes are normally monitored infrequently and analysis of indicator parameters is emphasized. Our experience at the North Bay site indicates this is adequate to establish a gross picture of the plume behaviour, but may be inadequate to discuss more subtle, but still significant, changes in contaminant concentrations. The temporal variability of contaminants should be evaluated. Before the concentration of an indicator parameter such as chloride can be used to infer the concentration of another contaminant, a strong correlation of these parameters must be shown throughout the plume. This is certainly not the case in the North Bay plume.

In addition, reactive contaminants are generally unlikely to remain well-correlated to non-reactive indicator parameters during transport. This is particularly true for organic contaminants which are undergoing biodegradation. To illustrate this, consider the decrease in chloride and benzene concentrations as groundwater moves down the flow system from G-5 to AAA-5 (see Tables 1 and 2). Whereas the chloride concentration decreased almost seven-fold, the benzene concentration decreased thirty-two-fold! This difference was typical over the 1984-86 data base. Barker et al. (1986) cautioned that such dramatic organic concentrations declines could not be directly interpreted in terms of the extent of biodegradation due to the considerable temporal variability of both chloride and benzene inputs from the landfill. However, even a caution interpretation of the differences between chloride and benzene decline must invoke biotransformation of benzene. In any case, the inability to predict organic contaminant concentrations from indicator parameter data is obvious.

A LANDFILL ON THICK CLAYEY DEPOSITS

The use of clay liners at waste disposal sites is frequently advocated as a means of minimizing the potential for groundwater contamination. It is commonly thought that if a clay liner has no structural defects and has a low hydraulic conductivity everywhere, the liner will provide a barrier between the waste and the hydrogeologic domain beneath the liner. Guidelines for the properties of clay liners commonly specify that the liner should have a hydraulic conductivity less than 1×10^{-7} cm s^{-1} so that the rate of hydraulic flow through the liner will be small. Advection of contaminants through the liner will therefore be slow. Even when advection is minimal, however, contaminants can migrate through clay liners at rates that may be significant. This non-advective migration is caused by molecular diffusion.

This paper describes an investigation of contaminant migration in a natural clay deposit beneath a completed cell at a hazardous waste-disposal site. The clay is unweathered and has a very low hydraulic conductivity ($< 10^{-8}$ cm s^{-1}). Because of the lack of weathering, uniformity and low hydraulic conductivity, the clay has all of the features normally desired of a clay liner. The purposes of the investigation are to determine the rates at which inorganic and organic contaminants from the waste migrate downward through the clay and to assess the applicability of simple diffusion models for predicting these rates.

The waste disposal facility, which is operated by Tricil Limited, is located 15 km southwest of Sarnia, Ontario. It is the only landfill in Ontario that receives hazardous wastes exclusively. We selected the site for this study primarily because the natural clay deposit is thick and therefore vertical boreholes through the waste could be drilled a metre or two into the clay without destroying the integrity of the overall deposit. From the bottom of the waste to the bedrock aquifer underlying the clay, the clay is 25 m thick. The site possesses additional attributes, such as waste material that offers no obstructions to drilling, accurate information on the locations and depths of old cells, and hydrogeological conditions that have been determined in detail in previous investigations.

The waste-disposal cell selected for this investigation was excavated in 1979. The cell received its final load of waste in 1980. The waste mass consists mainly of fly ash from a nearby coal-fired electrical generating station. Liquid hazardous wastes were mixed with the fly ash prior to disposal. The cell has a 2 m thick cover of compacted clay.

The study site is situated on a flat clay plain that extends more than 20 km in all directions from the site. The clay deposit which is late Quaternary in age, was formed by glaciers that protruded into a large glacial lake. The deposit contains numerous small pebbles and granules of shale bedrock indicative of the glacial-till origin of the deposit. About 40% of this glacial till is clay-sized particles, which are primarily illite and chlorite (Quigley and Ogunbadejo, 1976). The remainder consists of silt and sand-sized material and a small percent of pebbles.

Desaulniers et al. (1981), and Desaulniers and Cherry (1986) have studied the permeability of the clay, and the flow rates and age of groundwater in the clay at several locations on the clay plain including the Tricil site. The investigators concluded that, below about 5 m from ground surface, the clay is unweathered, has an average hydraulic conductivity less than 5 x 10^{-8} cm s^{-1}, has downward groundwater flow at average linear velocities less than several millimetres per year, and contains water that is very old, generally many thousands of years old. They also concluded that natural solutes in the groundwater, such as Cl^-, Na^+, ^{18}O and ^{2}H have developed vertical concentration profiles dominated by the influence of molecular diffusion during the geologic time. Desaulniers et al. (1986) simulated the vertical concentration profiles by means of one-dimensional diffusion models and diffusion times of 9,000 to 16,000 years.

From analysis of core samples taken from weathered clay at the bottom of a municipal landfill in Sarnia, Goodall and Quigley (1977) and Crooks and Quigley (1984) determined vertical profiles of several inorganic leachate-derived constituents. While the data suggest diffusion as the dominant cause of profile development, they only had limited success in the fitting of a diffusion model to the data. Our investigation has some similarities to the work done by Quigley and co-workers, but our focus is on the clay at greater depth where it is unweathered and on organic compounds rather than inorganic compounds other than chloride.

After sectioning the cores, pore water obtained by squeezing numerous core segments was analysed for chloride and volatile organic compounds. Chloride was detected in the clay to a maximum depth of 90 cm below the bottom of the waste. The most mobile organic compounds were found only to a depth of 25 cm. Although there is a large downward hydraulic gradient in the clay, the downward migration of chloride is caused only by molecular diffusion without significant influence by advection. The smaller distances of penetration for the volatile organic compounds are attributed to adsorption. Because the clay deposit is 20 m thick, it will take thousands of years for contaminants to diffuse through the clay into the underlying aquifer. This study has implications with respect to low-permeability clay liners used at waste disposal sites. The results of this study suggest that for liners of typical thickness (< 1 m), molecular diffusion will cause breakthrough of relatively mobile contaminants in several years or less. The details of this investigation are provided in a paper by Johnson et al. (1986).

CONCLUSIONS

Landfill sites on permeable materials provide a temporally-variable input of contaminants to shallow groundwaters. Groundwater transport processes seem to establish leachate plumes which have far-less variability of extent and shape based on the distribution of indicator parameters. However, it appears that trace organic contaminants still show considerable temporal variability in the groundwater flow system. Also, their concentrations are poorly predicted from the concentration of indicator parameters such as chloride. This is due, in part, to the variability of the input of contaminants from the landfill. Whereas transport processes such as dispersion may act to smooth the input variability, processes such as biodegradation render the relationship between chloride and organic contaminants far less regular.

Molecular diffusion is the dominant transport process at landfill sites on unfractured impermeable clayey deposits. Thus leachate plumes are far more restricted. Organic contaminants appear to migrate even slower than conservative tracers such as Cl, due to sorption. Diffusion-dominated transport is sufficiently slow to provide considerable protection of aquifers at the site on clayey till. However, the protection afforded by thin clay liners is probably far briefer.

REFERENCES

Barker, J.F. (in press). Volatile aromatic and chlorinated organic contaminants in groundwater at six Ontario landfills. Water Poll. Res. Jour. Can.

Barker, J.F., J.A. Cherry, J.P. Greenhouse, N.E. Gensky, M. Moore, M.M. Zapico and D.A. Carey, 1985. Organic contaminants at four Ontario landfills.

Barker, J.F., J.A. Cherry, D.A. Carey, J.P. Hewetson, J.F. Pankow, and M. Reinhard, 1984. Organic contaminants in groundwaters at several Ontario landfills. Proc. MOE Technol. Transfer Conf. no. 5, Part 1, Toronto, November 1984, Ontario Ministry of the Environment, 49-68.

Barker, J.F., J.S. Tessman, P.E. Plotz, and M. Reinhard, 1986. The organic geochemistry of a sanitary landfill leachate plume. Jour. Contaminant Hydrol., 1, pp. 133-142.

Crooks, V.E. and R.M. Quigley, 1984. Saline leachate migration through clay: a comparative laboratory and field investigation. Can. Geotechn. J., Vol. 21, no. 2, pp. 349-362.

Desaulniers, D.E., J.A. Cherry and P. Fritz, 1981. Origin, age and movement of pore waters in argillaceous quaternary deposits at four sites in southwestern Ontario. Journal of Hydrology, Vol. 50, pp. 231-257.

Desaulniers, D.E. and J.A. Cherry. Origin and movement of groundwater and major ions in a thick deposit of Champlain Sea clay near Montreal, Quebec. Canadian Geotechnical Journal (submitted April, 1986).

Desaulniers, D.E., R.S. Kaufmann, J.A. Cherry and H.W. Bently, 1986.

^{37}Cl- ^{35}Cl variations in a diffusion-controlled groundwater system. Geochimica et Cosmochimica Acta, Vol. 50, pp. 1757-1764.

Goodall, D.C. and R.M. Quigly, 1977. Pollutant migration from two sanitary landfill sites near Sarnia, Ontario, Can. Geotechn. J., Vol. 14, pp. 223-236.

Johnson, R.E., J. Pankow and J.A. Cherry, 1986. Diffusion of chloride and volatile organic contaminants in clay beneath a hazardous waste disposal site. Submitted To: Env. Sci. and Technology (Oct. 1986).

Mackay, D.M., J.A. Cherry, D.L. Freyburg, G.D. Hopkins, P.L. McCarty, M. Reinhard, and P.V. Roberts, 1983. Implementation of a field experiment on groundwater transport of organic solutes. Presented at the Groundwater Contamination Session of the 1983 National Conference on Environmental Engineering, ASCE, University of Colorado, Boulder, Colorado, July.

Moore, M.B., 1986. An investigation of the permeability of a sand aquifer to determine the contaminant mass flux of selected contaminants from a landfill plume. M.Sc. Thesis, University of Waterlo, Waterloo, Ontario.

Patrick, G.C. and J.F. Barker, 1985. A natural-gradient tracer study of dissolved benzene, toluene, and xylene in groundwater. Proc. Second Annual Can./Amer. Conf.Hydrogeol.: Hazardous Wastes in Ground Water--A Soluble Dilemma, June 25-29, 1985, Banff, Alberta, pp. 141-147.

Quigley, R.M. and T.A. Ogumbadejo, 1976. Till geology, mineralogy and geotechnical behaviour, Sarnia, Ontario: Proceedings of the Conference on Glacial Till, Royal Soc. Can. Special Pub. No. 12, R.F.

Legget (ed.), p. 336-345.

Reinhard, M., N.L. Goodman, and J.F. Barker, 1984. Occurrence and distribution of organic chemicals in two landfill leachate plumes. Environ. Sci. and Technol. 18, pp. 953-961.

Sudicky, E.A., J.A. Cherry, and E.O. Frind, 1983. Migration of contaminants in groundwater at a landfill: a case study. 4. a natural-gradient dispersion test. Jour. Hydrol. 63, pp. 81-108.

Sutton, P.A. and J.F. Barker, 1985. Migration and attenuation of selected organics in a sandy aquifer--a natural gradient experiment. Ground Water 23, 10-16.

Table 1:

Inorganic Parameters in Groundwater from the North Bay Landfill Leachate Plume. Concentrations are in mg/L Unless Noted Otherwise. Samples Collected 21/11/83

Parameter	**Piezometer**			
	G-5	**LL-5**	**LL-9**	**AAA-5**
pH	6.9	6.8	6.7	6.4
Conductivity (umho/cm)	4510	1740	2650	560
Ca	232	106	123	50.0
Mg	99	37.5	56	14.4
Na	285	109	197	38
K	230	56.5	81.5	11.0
Alkalinity (as $CaCO_3$)	2070	711	970	220
F	0.06	0.06	0.04	0.04
Cl	332	138	226	50.0
SO_4	15.0	8.0	13	10.0
NO_3 (as N)	<0.1	<0.1	<0.1	<0.1
Kjeldal N (as N)	192	53.5	76.0	12.0
Ammonium (as N)	185	47.5	68.0	7.0
Nitrite (as N)	0.06	0.06	0.08	0.06
DOC	129	46.5	82.0	12.9
Fe	82	90	140	22
Mn	5.6	5.6	8.2	3.4
As (ug/L)	< 1	2	2	1
Ba "	220	1500	2600	270
Cd "	<10	<5	80	<5
Cr "	33	23	38	11
Cu "	<9	<5	<5	<5
Ni "	79	63	100	21
Pb "	67	88	160	<30
Se "	<1	<1	<1	<1
Zn "	6	9	11	8

Table 2: Selected Organic Parameters in Groundwater from the North Bay Landfill Leachate Plume. Concentrations in ug/L Unless Noted Otherwise.

Parameter	**Piezometer**		
	G-5	**LL-9**	**AAA-5**
MOE Lab (20/11/83)			
Lindane (ng/L)	1	<1	<1
Dieldrin "	<1	4	2
DDD "	<5	25	<5
Biphenyl	3	1	n.d.
Polyethylene Glycol Deriv.	180	10	n.d.
Dimethylbenzoic Acid	n.d.	13	n.d.
Tributyl Phosphate	22	15	2
Phthalates	110	50	10
Phenols	10	15	n.d.
Hydroxybenzothiazole	10	<15	3
Chloroform	0.9	-	n.d.
1,2-Dichlorobenzene	13	14	3
Acetone	6	2.4	0.6
Diethyl Ether	15	20	4
Tetrahydrofuran	9	5	0.6
Methyl Ethyl Ketone	2	0.8	n.d.
Thiophene	0.6	n.d.	n.d.
1,4-Dioxane	0.6	n.d.	n.d.
Diethyl Sulphide	3	n.d.	n.d.
Hexanol	11	6	n.d.
Fenchone	48	27	n.d.
Camphor	19	n.d.	n.d.
UW Lab (26/10/84)			
Benzene	51	13	1.6
Toluene	1.3	n.d.	n.d.
Chlorobenzene	9.1	6.9	n.d.
Ethylbenzene	58	13.6	n.d.
p-Xylene	90	-	n.d.
o,-m-Xylene	7.6	-	n.d.
Cumene	6.6	2.8	n.d.
1,2,4-Trimethylbenzene	51	2.7	n.d.
Napthalene	15	n.d.	n.d.

Table 3: Slope (m) and Intercept (c) for the Relationship Between Chloride and Various Organic Concentrations, Where Organic = m x chloride + c. The linear Correlation (Coefficient of Correlation r) Between Chloride and Organics is also shown.

Location	Organic	No. of Data	Slope (m)	Intercept (c)	Linear Correlation (r)
G	Benzene	66	1.30	31.0	-0.0968
	Chlorobenzene	66	2.51	13.8	0.0231
	1,2,4-Trimethylbenzene	66	-0.145	90.6	-0.511
LL	Benzene	72	-0.0643	-0.13	0.773
	Chlorobenzene	72	0.0551	1.78	0.622
AAA	Benzene	21	-1.18	1.61	-0.113

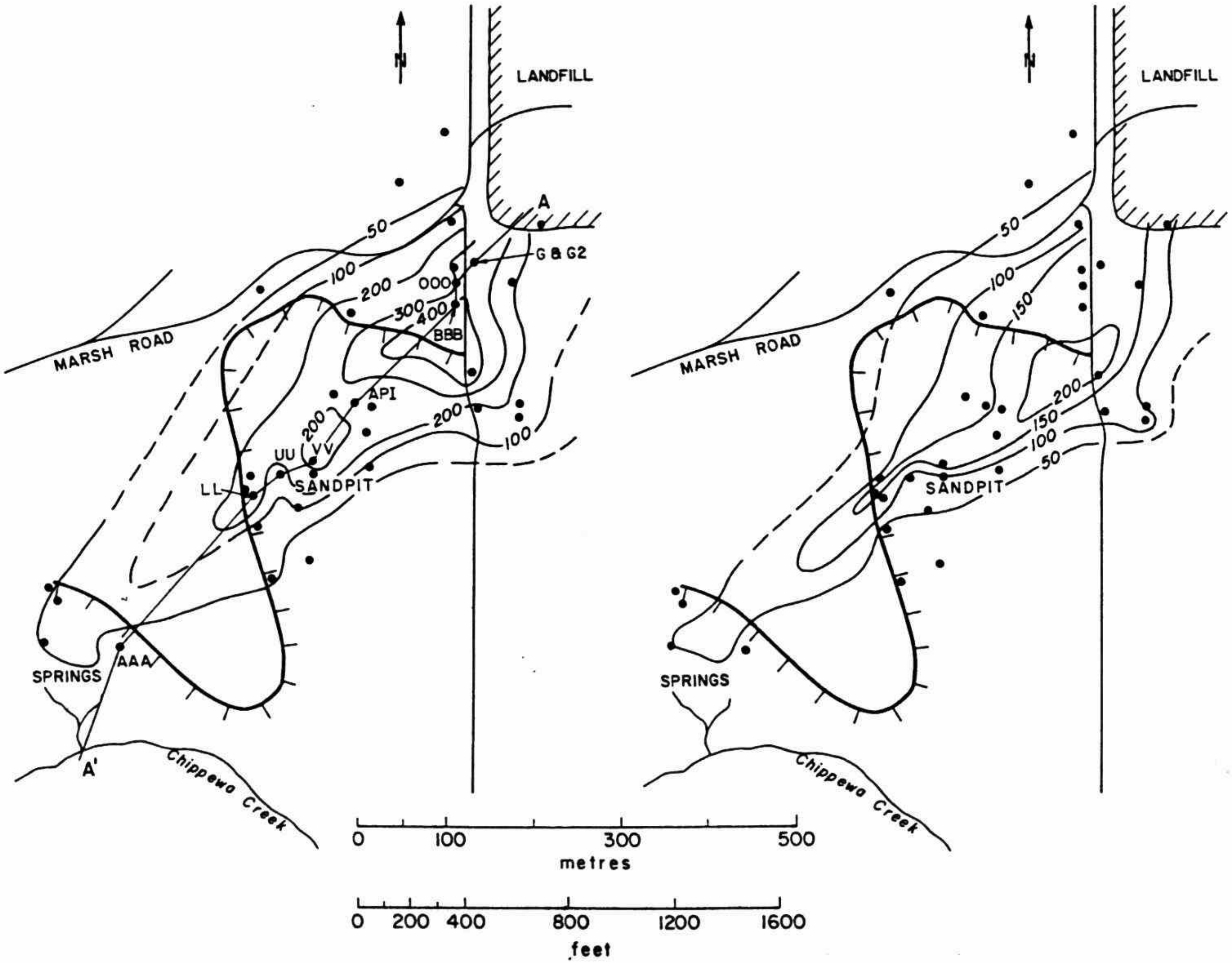


Figure 1. Plan view of the North Bay Landfill Leachate Plume. The maximum chloride (left) and TOC (right) concentrations at each multilevel piezometer for 1982 are contoured.

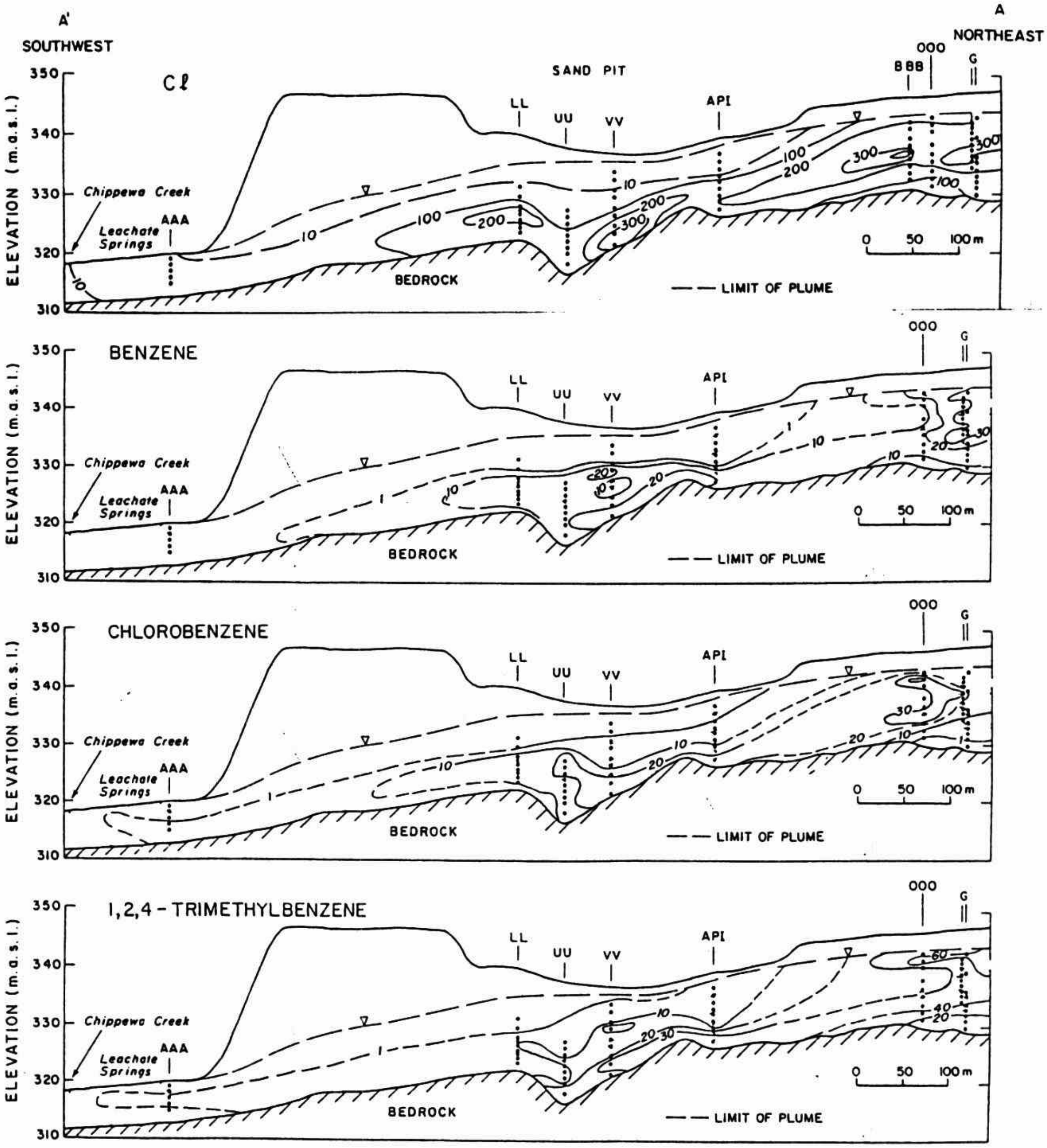


Figure 2. Chloride, benzene, chlorobenzene and 1,2,4-trimethylbenzene distributions along cross-section A-A'. Contoured from July, 1985 data.

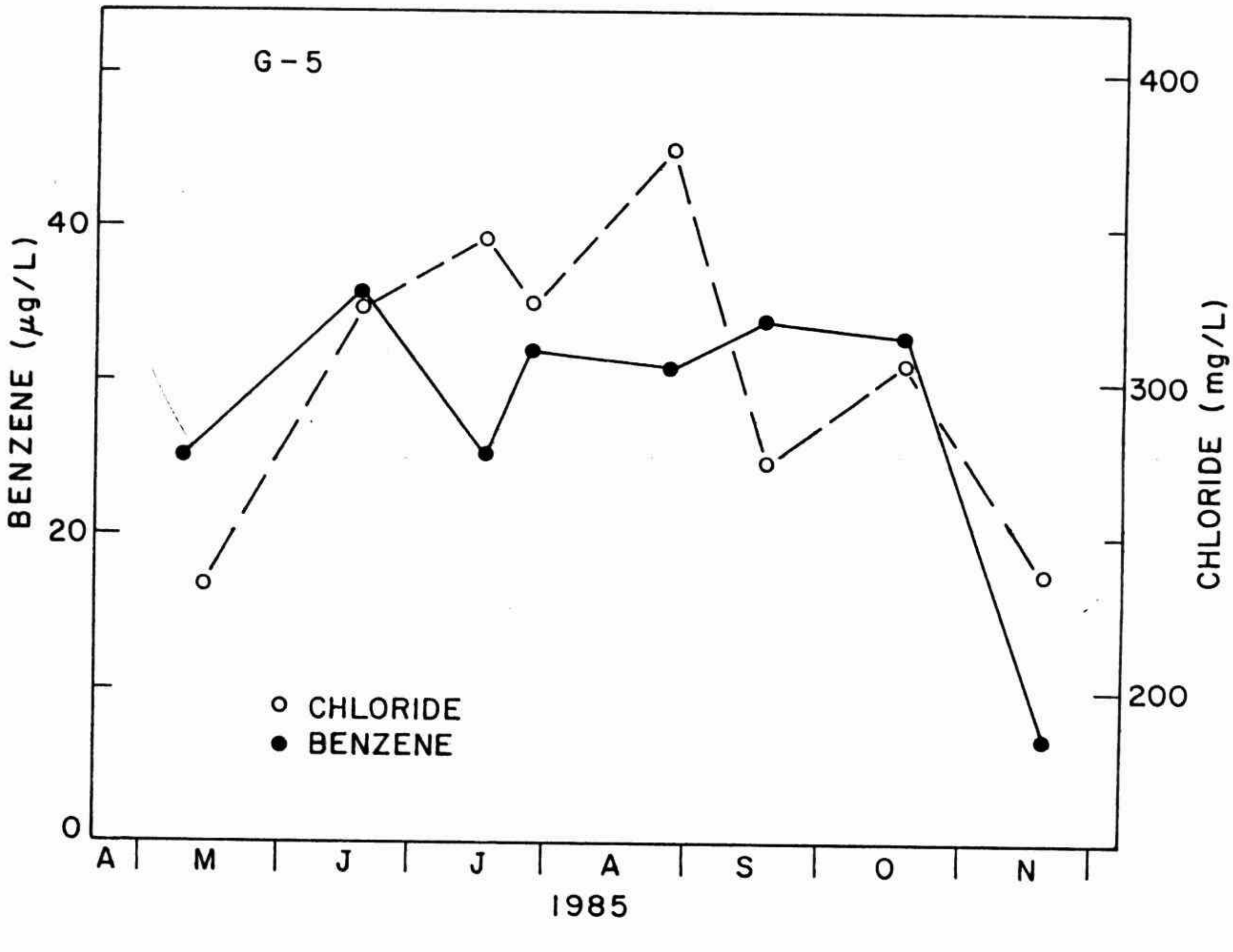


Figure 3. Temporal variation (1985) for chloride and benzene concentrations in groundwater from piezometer G-5, near the landfill.

DISPERSION OF THE STOUFFVILE CONTAMINANT PLUME

I. Proulx, R.N. Farvolden and E. Frind,
University of Waterloo,
Waterloo, Ontario

DISPERSION OF THE STOUFFVILLE CONTAMINANT PLUME

Introduction

The Oak Ridges aquifer complex is a source of large quantities of high quality water. These sand and gravel aquifers underly much of the Oak Ridges moraine on which the Stouffville landfill site is located (Fig. 1). Variations in groundwater quality parameters over the years show that a plume of contamination has developed in the aquifer under the landfill. The objective of this paper is to describe the complex physical and hydrogeological setting at this site and begin to interpret the observed variations in groundwater quality caused by plume evolution.

Waste disposal activities

Operations at the landfill site began in 1962. No accurate records of the nature or the quantity of wastes disposed of at the site are available before 1974. However, some facts are known about disposal activities at the site in the early years. Both liquid industrial wastes and solid wastes were received until 1970. The liquid wastes were disposed of on top of the solid wastes and covered with earth in the south and southwest areas. Natural depressions formed by glacial processes were also used for the disposal of liquid wastes (Fig. 2). After 1970 only solid municipal wastes were accepted at the site. The depressions used for liquid waste disposal were filled with solid wastes in 1973-74 and then buried by waste and cover material. The site was closed in July 1985 after millions of tons of waste had been received.

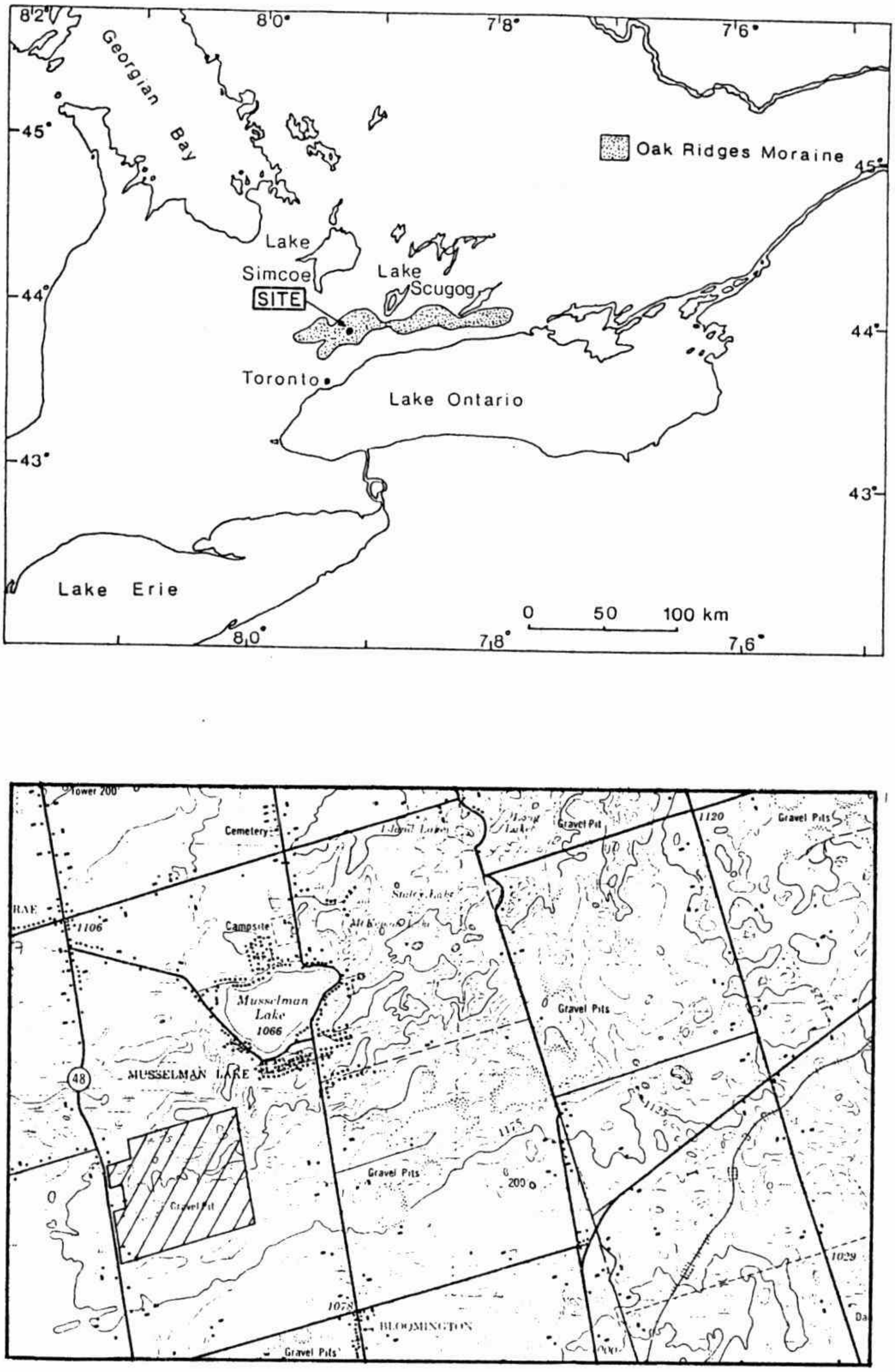


Figure 1: Location map

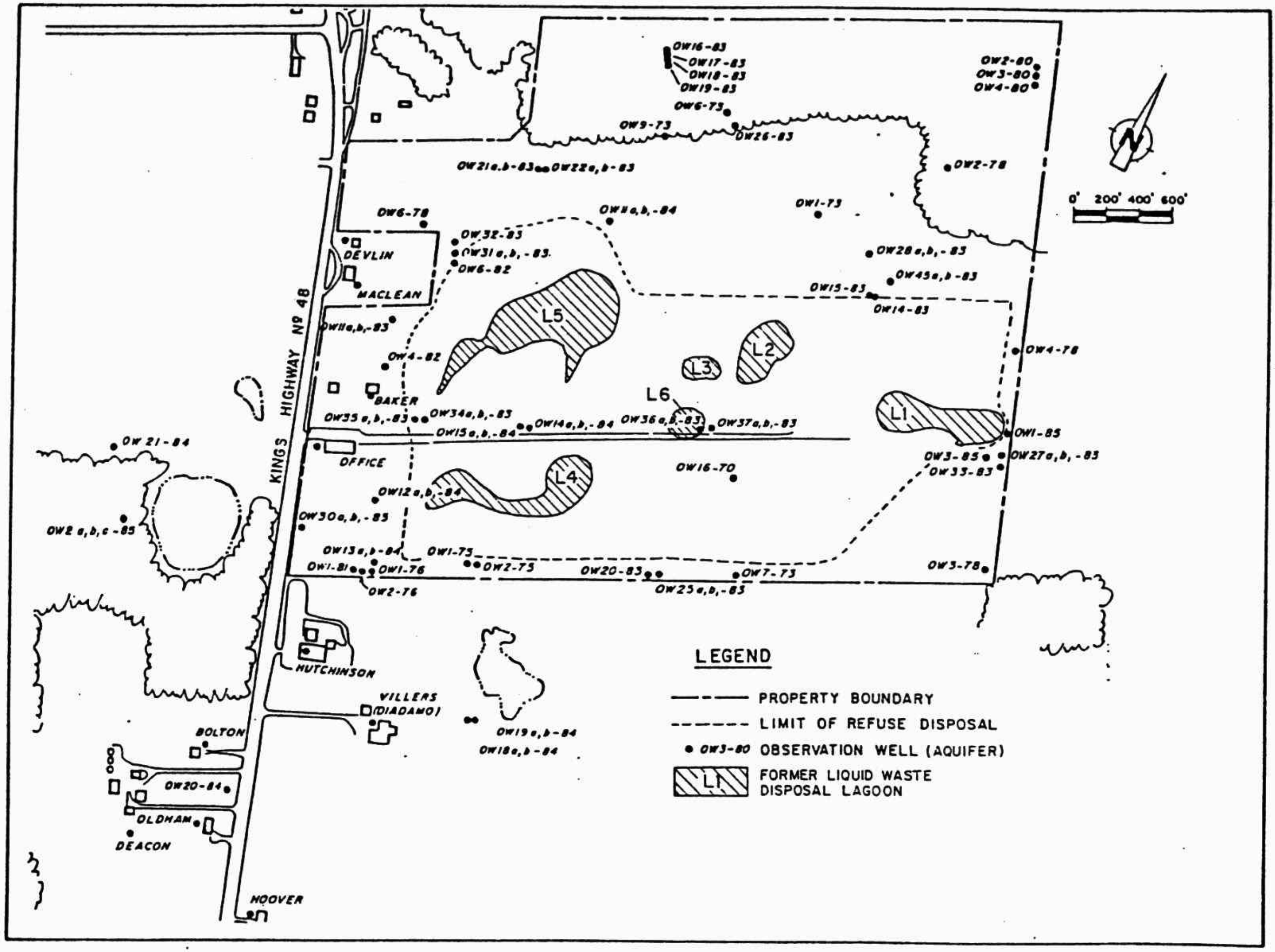


Figure 2: Aquifer observation wells and disposal lagoons

(Modified from WMI, 1985)

Quaternary Geology

A recent study in the Musselman Lake area (Kaye, 1986) led to an improved understanding of the local depositional history and hydrostratigraphy.

Advances and retreats of Late Wisconsinan glacial ice are responsible for the different types of deposits formed in the area. Till units were formed during ice advances, while retreats resulted in deposition of outwash sands and gravels.

The first record of glacial advance is the group of tills and glaciolacustrine units observed in the deepest holes on site. The sand and gravel aquifers underlying the site was formed during the subsequent ice retreat. A second ice advance followed and generated the fine grained Halton till, south of Musselman Lake. An unconfined glacio fluvial aquifer was formed to the north of Musselman Lake during the last ice retreat. See Figure 3 for illustration of simplified stratigraphy of the area.

Site description

Previous investigations of the site (WMI, 1985) used logs from observation wells and borehole resistivity logs from 17 deep holes to define the hydrostratigraphy under the site. Five units were identified.

The uppermost unit is thin and discontinuous in the north part of the site, but reaches a 20 m thickness to the west. The composition of this sediment, known as the Halton till, varies from a very clayey to a very sandy silt diamict. Hydraulic conductivity values of 1×10^{-2} to 3×10^{-7} cm/s were obtained from grain size analyses using the Hazen method. This wide range illustrates the diversity of materials forming the unit. Local perched water table systems are found associated with the impermeable material, but at several places, the Halton till is unsaturated throughout.

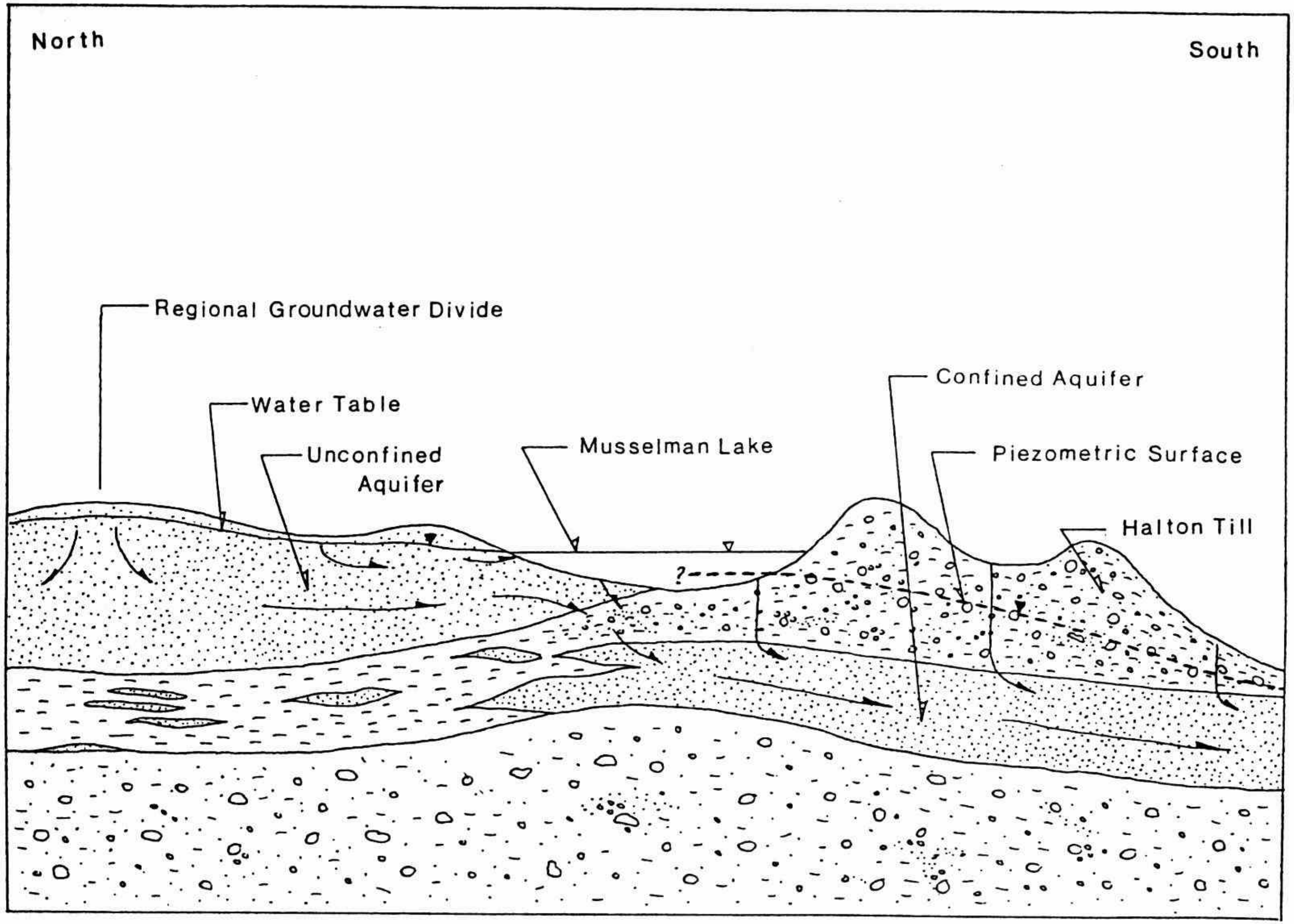


Figure 3: Local stratigraphy and flow pattern

(From Kaye, 1986)

Below the Halton till is the main sand aquifer of glacio fluvial origin. This heterogeneous unit consists of beds and lenses of clay, silt and gravel in fine to medium grained sand. The 30 to 60 m thick aquifer is unconfined in the northernmost part of the site, but is overlain by the Halton till over the remainder of the site, and elsewhere in the region. A thick unsaturated zone occurs between the Halton till and the water table under the site.

Three fine-grained deposits acting as aquitards underly the aquifer at different places below the site and for practical purposes, represent the bottom of the flow system.

Hydrology of the Halton till

Driller logs of holes penetrating the Halton till show highly variable stratigraphy. These complex conditions result in different infiltration rates over the site. Some observations are indicative of generally impermeable conditions: thick unsaturated zone, numerous locations of ponding and perched water, and very stable aquifer well hydrographs. Conversely, the existence of some permeable areas is indicated by a minimal amount of runoff from the site before it was altered, and the rapid infiltration of the liquid wastes in the disposal 'lagoons'. Also, several dry zones occur in the unit, indicating recharge conditions.

Comparison of hydrographs and water quality data for shallow wells suggest poor hydraulic connections between the local zones of perched water in the Halton till. Strong vertical gradients and discontinuity of the perched groundwater zones in the till (Fig. 4) are good evidence that the hazard for off site contamination through the Halton till is minimal.

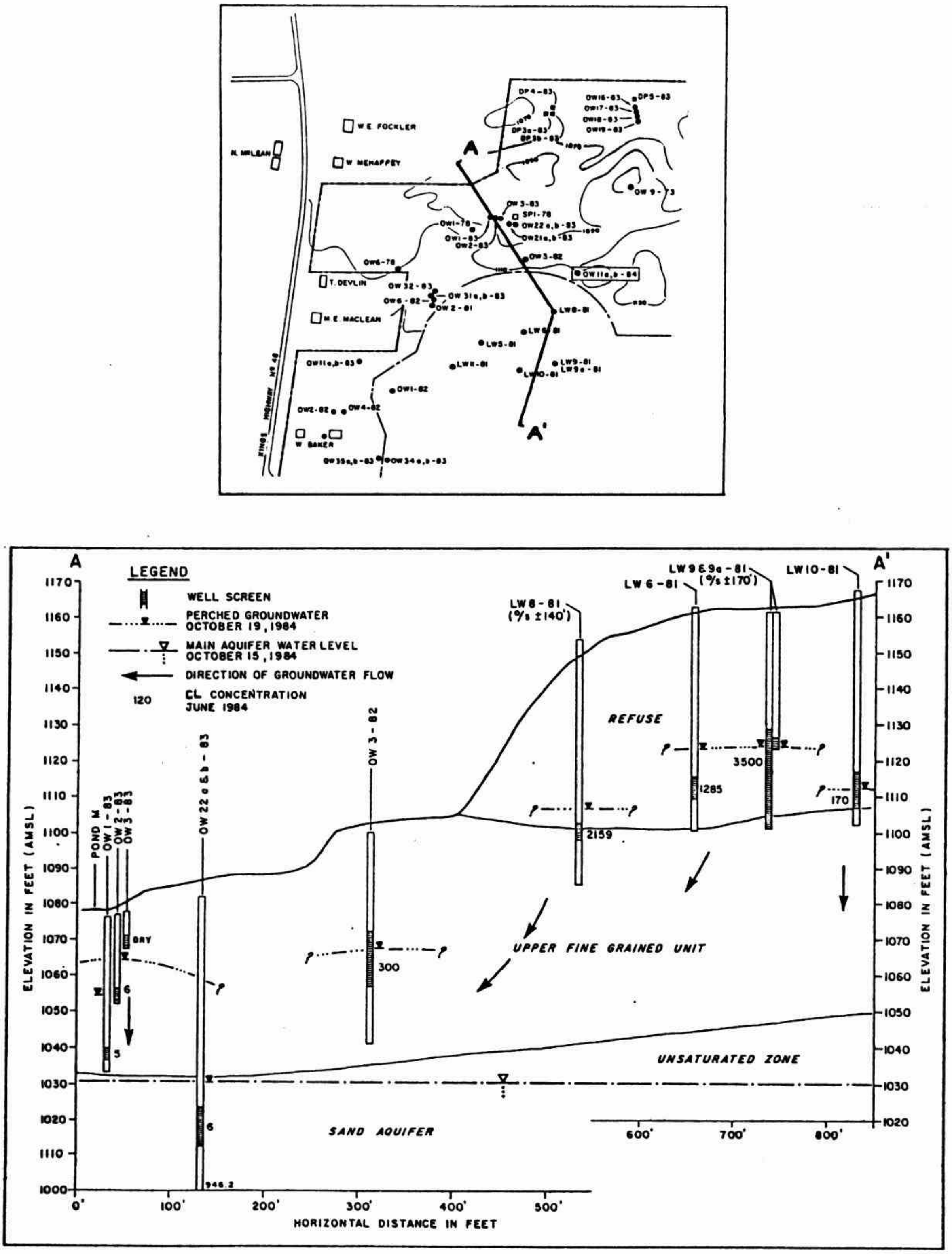


Figure 4: Perched water in the north slope

(Adapted from WMI, 1985)

Flow in the main aquifer

Regional groundwater flow is to the southwest with a regional horizontal hydraulic gradient on the order of 0.012 (WMI, 1985). In places directly under the site values as low as 0.004 are observed.

Kaye (1986) came to the conclusion that Musselman Lake was receiving recharge from the northern unconfined aquifer, while acting as a reservoir to the southern aquifer. This constant source of recharge to the southern aquifer, augmented by infiltration from land surface, maintains the mass flux between the landfill and the site through the year.

Equipotentials configuration on site fluctuates seasonally and indicates local recharge. A depression for storage of storm water at the northeast corner of the property acts as one obvious recharge zone (Fig. 5).

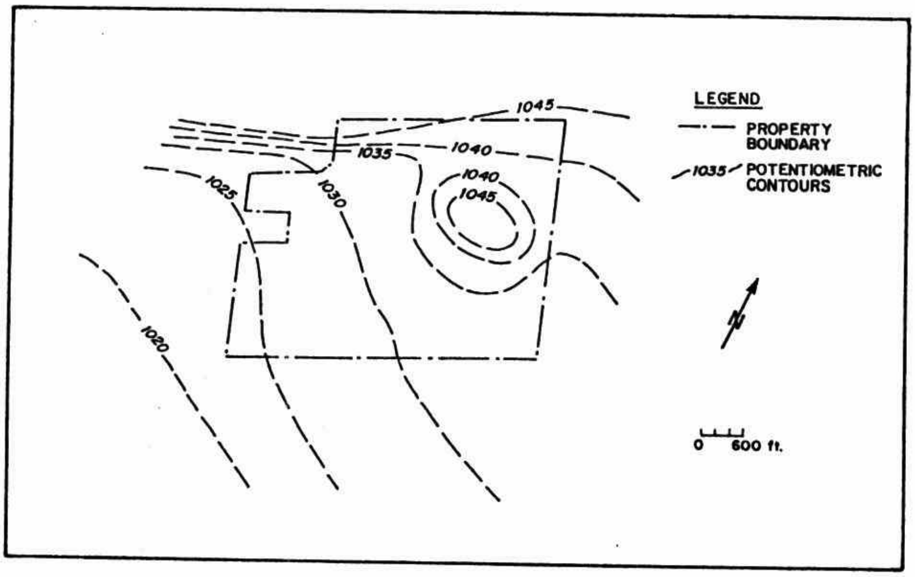


Figure 5: Isopotentials in main aquifer

(October, 1984)

During the spring, circular isopotentials of a water table mound can be drawn under this zone. In the winter the mound decays and isopotentials have a curvilinear shape. This recharge mound has a strong, although temporary, influence on the direction of groundwater flow in the main aquifer, disrupting the normal flow pattern and producing off site gradients that must be considered in an analysis of contaminant migration.

Monitoring program

In the period from 1970 to 1985, 96 observation wells, 25 test holes, 22 boreholes, and 21 leachate wells were installed at the site. The main aquifer was penetrated by 38 of these installations consisting of standpipe piezometers or nests of 2 or 3 piezometers spread over the aquifer thickness. Ten domestic wells are located on or very close to the site. The earliest groundwater quality data were obtained in 1968 from the Hutchinson domestic well, and at that time chemical analyses were limited to chloride, conductivity, phenols and sulphate.

In November 1981, a university laboratory reported bacterial mutagenicity in the water of a private well adjacent to the landfill site. This brought about the initiation by the Ministry of the Environment (MOE) in December 1981 of an in-depth chemical and biological study of the site. The final report was completed in November 1982 and no bacterial mutagenic activity was identified. It was also concluded that there were no evidence of off site contamination by the industrial organics present in the landfill (MOE, 1982).

From 1982 to 1984 a hydrologic investigation was conducted by Conestoga Rovers and Associates for the site owner, WMI, as a condition for completion of activities and closing of the landfill site. The resulting report is available at the MOE and the Town of Stouffville. Since the initiation of that study, a monitoring program in which some 50 points are sampled every three months is being conducted. The water samples are analyzed for selected indicator parameters.

Discussion

The Halton till on the site contains the refuse, and thus considerable contamination. This contamination may be reaching the main aquifer, but it does not appear to migrate significantly off site in the local perched water systems of the till unit.

No generalization can be made concerning the hydraulic properties of the Halton till, except that they are highly variable at the site. As an alternative to an impracticle attempt to characterize infiltration rates through the Halton till, this unit at the site is considered as a potential contaminant source whose impact would first be recorded at the water table of the main aquifer. Therefore the contamination reaching the water table is treated as the contaminant input function to the flow system. The regional groundwater flow system and main aquifer characteristics under the site have been determined. Plumes of contamination in the main aquifer can be drawn (see Fig. 6), and studies to delineate the exact configuration and size are in progress.

Two different hypotheses as to the cause of the observed historical water quality variations exit. Consecutive peaks observed in wells at increasing distance from the lagoons are seen as evidence of the fast migration of water contaminated by liquid wastes. The graph of historical chloride concentration variations has the same general shape as the arrival curve of a dispersed contaminant front. A different interpretation would be that the liquid waste produced these historical chloride arrival curves, and their peaks. Preliminary computer simulations of this possibility were performed using an analytical solution for 2-D transport from a

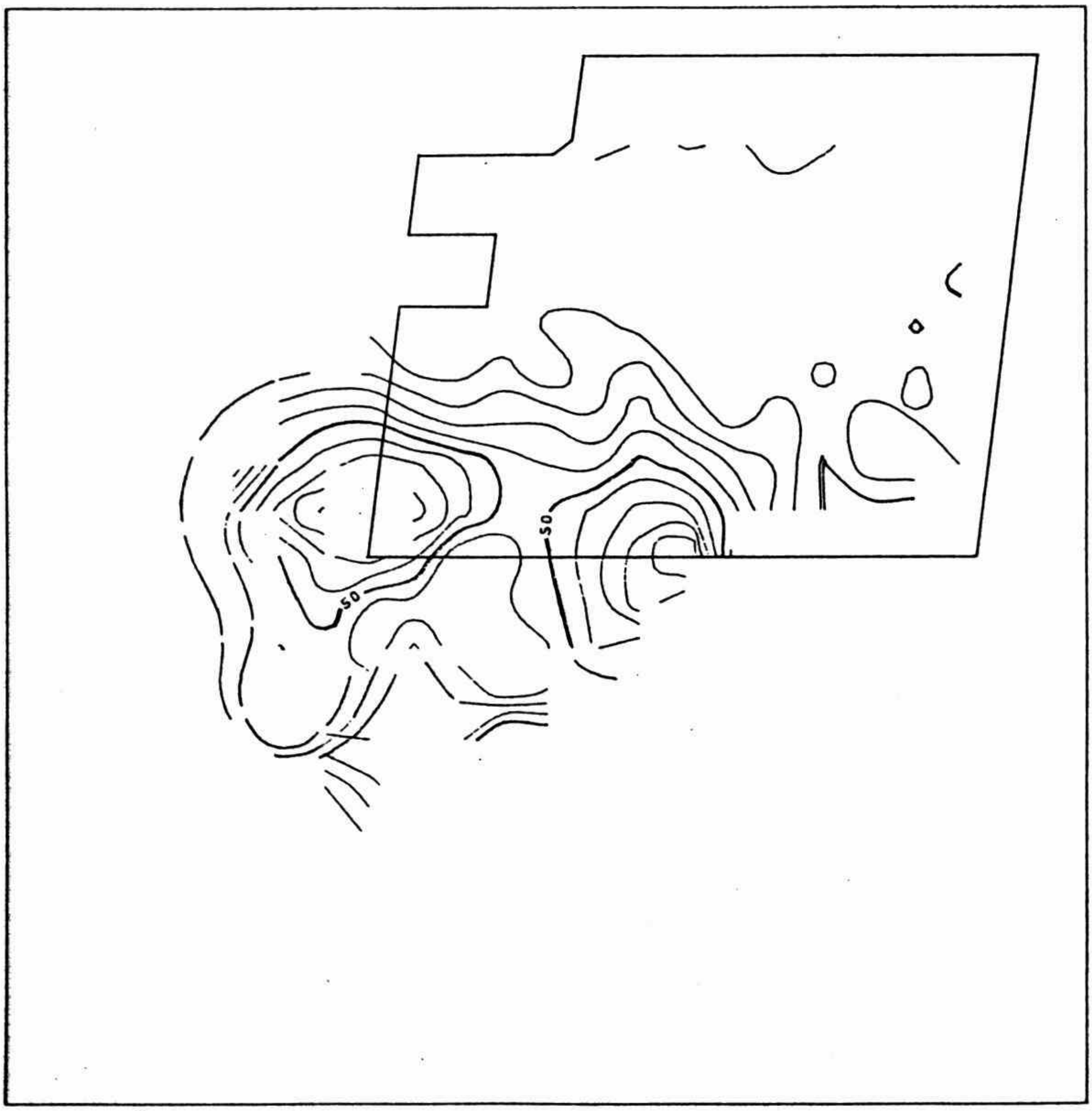


Figure 6: Chloride plume in main aquifer

May 1985 - Contour interval of 10 mg/l

line source (Sudicky, 1986). The regional dispersivity value of 20 observed in glacial deposits of Long Island (Anderson, 1979) was used. A relatively small velocity of 25 m/y was required to simulate the historical curves. The general shape of the observed curve, and its time span between first arrival of concentrations higher than background and a relative stabilization of concentration could be reproduced at different locations.

Historical water quality variations reach a relative level of stability. The record of water quality variations in the younger wells (1983-85) is shorter, but values of the indicator parameters seem relatively stable. The volume of aquifer of concern is quite large, and uncertainties about the degree of control on the plume can be raised, but up to date observations do not reflect fast off site plume migration.

Three-dimensionnal computer simulations of variable to constant in time inout at the water table would help to understand how the contamination plume has developped.

Conclusions

The regional and local hydrogeologic environment of the landfill site have been described. No significant off site contaminant migration occurs in the Halton till. The till is generally impermeable, but permeable pathways exist under the site resulting in contamination of the main aquifer. Up to date results from the monitoring program indicate that the plume of contamination does not extend far from the site.

The drilling of additional holes in the main aquifer is planned for this year to increase control on plume delineation. More work on the chemical data base is in progress to determine the proce sses influencing plume development. More involved transport modelling will be accomplished.

References

Anderson, M.P., 1979. Using models to simulate the movement of contaminants through groundwater flow systems in CRC Critical Reviews in Environmental Control, vol. 9, issue 2, November 1979.

Conestoga Rovers and Associates Ltd., 1985. Hydrogeologic study program, Canadian landfill division, Sanitary Landfill Site No. 4, Waste Management of Canada Inc. Ref. No. 1187-5.

Kaye, B.G., 1986. Recharge characteristics of the Oak Ridges Aquifers Complex: the Role of Musselman Lake. M.Sc. Thesis, University of Waterloo.

Ontario Ministry of the Environment, 1982. Whitchurch-Stouffville Groundwater Chemical Testing Program, Final Report, 144 p.

Ontario Ministry of the Environment, 1982. Hydrogeologic Assessment of York Sanitation Company Limited Waste Disposal Site No. 4, 113 p.

DEVELOPMENT OF DESIGN CRITERIA FOR OPTIMAL COLLECTION OF LEACHATE UNDER SANITARY LANDFILLS

SUBMITTED TO:

Research Advisory Committee
Ontario Ministry of the Environment
135 St. Clair Avenue West, 12th Floor
Toronto, Ontario
M4V 1P5

SUBMITTED BY:

L. St. Arnaud, E.O. Frind,
R.N. Farvolden and R.W. Gillham

Institute for Groundwater Research
Department of Earth Sciences
University of Waterloo
Waterloo, Ontario
N2L 3G1

NOVEMBER, 1986

DEVELOPMENT OF DESIGN CRITERIA FOR OPTIMAL RECOVERY OF LEACHATE UNDER SANITARY LANDFILLS

L. St. Arnaud, E.O. Frind, R.N. Farvolden and R.W. Gillham
Institute for Groundwater Research,
Department of Earth Sciences, University of Waterloo.

ABSTRACT

A two-dimensional finite element model was used to study the effectiveness of tile drain systems for capturing leachate under unlined sanitary landfills. Computed steady-state conditions were compared with data produced from a laboratory model. Simulations were conducted for a simplified drain system with varying vertical hydraulic gradients, drain depth, thickness of the flow field, drain spacing, and leachate production rate. Results showed that most of the leachate can be collected if an upward vertical gradient exists beneath the drain level. If the vertical gradient is downward, the drains have to be very closely spaced in order to collect the leachate. Drain performance depends on the rate of recharge of leachate into the system, which partly controls the height of the groundwater mound between the drains. Optimal conditions can be attained when all the leachate is collected with minimum infiltration of groundwater coming from depth.

Introduction

In humid and sub-humid regions, the production of leachate is an inevitable consequence of the interaction of infiltrated water with buried waste. Leachate characteristically contains concentrations of dissolved matter far in excess of drinking water standards. Preventing the contamination of groundwater by landfill leachate is a major consideration in landfill design. The key factor in avoiding serious contamination is the proper placement of the landfill, which should be done by taking in account the groundwater flow directions, the hydrogeological properties of the subsurface materials and the proximity of aquifers and surface water bodies. In addition, the leachate production rates have to be evaluated and controlled. A common practice to achieve this is by the use of leachate collection systems placed at the bottom of the landfill. These systems are usually composed of drain networks. In many cases, clay liners are used to hydraulically isolate the landfill from the underlying geological material.

Several mathematical models to evaluate the effectiveness of leachate collection are available in the literature. However, these models were not developed for cases where, in order to avoid the high costs of liner construction, proposed leachate collection systems consist solely of a tile drain network.

The purpose of this study is to determine a method suitable to evaluate the efficiency of tile drain systems for collecting leachate without the use of liners. The work described is part of a three year research project funded by the MOE lottery fund. In a previous report (Farvolden et al., 1985) experiments with a laboratory model were described. Parallel to these experiments, a two-dimensional finite element numerical model was applied to a simple system similar to the one modelled in the laboratory. Results of this work were summarized in Abdul et al. (1985). The present report discusses the results produced by the two previous studies and describes the progress made towards the application of the numerical model to more general hydrogeological situations.

MATHEMATICAL MODELS TO EVALUATE LEACHATE COLLECTION

Figure 1 shows three different leachate collection system geometries studied in the literature. For a horizontal clay liner of zero permeability (Figure 1a), the following equation from Harr (1962) has been used to describe the shape of the groundwater mound on top of the liner:

$$h = (R/K\ (L - x)\ x)^{1/2}$$

where L is the distance between the drains, K is the horizontal hydraulic conductivity of the drained medium, R is the steady-state rate of leachate input into the system, and x is the horizontal distance from the drains. From this equation, it can be shown that: (1) the maximum height of the water table above the level of the tile drain increases as the recharge increases and/or the hydraulic conductivity decreases, and (2) the maximum height of the water table increases as the distance between the drains decreases.

McBean et. al. (1982) derived an equation for a sloped liner (1b) and presented a case study where the concern is the change of height of the groundwater mound for different steady-state recharge fluxes. McBean et al. (1982) suggested the use of their model to study alternative designs of leachate collection systems with respect to drain spacing and groundwater mounding.

An elaborate attempt to study the design of leachate collection systems is the one by Wong (1977). He developed equations to approximate the movement of a volume of water moving over the surface of a sloped clay liner towards a collector tile (figure 1c). Leakage through the liner and collection efficiency are expressed as a function of liner slope (θ), liner thickness (d), leachate head buildup (h), leachate flow distance (S), and hydraulic conductivities of the liner (K_2) and the material overlying it (K_1). Wong's model has been used for many practical design problems. His assumptions were:

1. The drainage layer overlying the clay liner has the same hydraulic conductivity as the refuse material
2. All materials are at field capacity, so that any infiltration of precipitation is transmitted to the bottom of the landfill
3. Pressure in the drain is zero
4. The leachate collection system is above the water table. Any effect of groundwater flow under the liner is neglected.
5. Leachate buildup appears instantly over the liner. The leachate saturates a rectilinear volume above the liner, and retains this shape while draining towards the collection drain and through the liner.

Kmet et. al. (1981) examined closely each one of Wong's assumptions and presented a sensitivity analysis based on Wong's model. They also presented a refinement of the method to estimate the value of the head buildup (h) after multiple recharge events. Dematrocopoulis et. al. (1984) give the most recent review of leachate collection models. They considered assumptions (1) and (5) of Wong to be controversial and presented a sensitivity analysis based on Wong's model, with modifications for time-variable leachate productions. Moore (1980) obtained leakage through the liner using Richard's equation for variably saturated flow. He also presented a methodology for evaluating the performance of leachate collection systems with liners.

In the case of leachate collection systems that do not include the low permeability liner, the natural hydrogeological conditions occuring under the landfill become important, and assumption 4 of the Wong model might not be applicable.

REVIEW AND DISCUSSION OF PREVIOUS WORK

Figures 2 shows a simplified view of what the hydrogeological conditions beneath the landfill might be. The landfill rests in a low permeability surface unit (clay or till) which overlies a second unit of higher permeability (aquifer). The flow system around the drains can be simplified to a 'half cell'. Figures 3 and 4 show the definition of the boundary conditions for the half cell system and the experimental apparatus used for the laboratory study. (Abdul et al., 1985, and Farvolden et. al., 1985). Table 1 defines the different parameters and dimensionless ratios that were used to study the half cell. In defining the system, the following assumptions were made:

1. The hydraulic conductivity of the landfill is the same as the hydraulic conductivity of the underlying porous medium.
2. All material beneath the drain level is saturated. The drains are thus below or at the natural water table level.
3. Recharge of leachate reaching the level of the drains is at steady state and is constant.
4. Any effect produced by the unsaturated zone above the drains is neglected.
5. Pressure in the drain is zero.
6. All flow occurs in a plane. Because a symmetrical flow field exists between the drains, no flow takes place across the side boundaries of the cell.

7. The landfill is built in a low permeability hydrogeological unit overlying an aquifer. This causes the hydraulic head at a certain depth beneath the landfill to be constant.

Both laboratory and numerical models of the half cell system were used to analyse the flow field around the drain by verifying the sensitivity of the flow field to changes in the values of recharge (R), hydraulic conductivity (K), hydraulic head at depth and at the drain (Ha,Hd) and half spacing between the drains. The results were presented in the form of response curves showing the variation of the value of Qa/Qr relative to dimensionless ratios R/K, Ha/Hd and Hd/L (figure 5). Qa is the total resulting discharge of water at the bottom of the system and Qr is the input discharge of leachate. Fluxes entering the system were considered positive and those leaving the system, negative. Consequently, the response factor Qa/Qr is related to the degree of leachate collection in the following way: as Qa/Qr increases (becomes more positive), leachate collection increases; as Qa/Qr decreases (becomes more negative) collection decreases.

The response curves show that leachate collection is higher in cases of upward vertical gradients (Ha/Hd>1) than in cases of downward gradients (Ha/Hd<1). In cases where vertical gradients are directed downward, the collection increases as R/K increases. When vertical gradients are directed upward, leachate collection increases as R/K decreases. In the particular case where no vertical gradients exist, leachate collection is only slightly dependent on changes in values of recharge or hydraulic conductivity.

A large positive value of Qa/Qr indicates that a large amount of water is infiltrating from the lower layer into the half cell system. The flownets of figure 6 are useful to visualize the different scenarios that can occur. In figure 6a, the ratio Ha/Hd is smaller than one, and most of the leachate is escaping through the bottom of the system. Figure 6b shows the conditions occuring when Ha/Hd equals 1.10: approximately half of the leachate is collected.

At least some of the leachate bypasses the drains in all the cases where Qa/Qr is smaller than zero. Figure 6c shows a situation that occurs when Qa/Qr is positive: most of the leachate is collected, but there is also a significant amount of water infiltrating from the bottom of the system. In this case, the value of Qd is equal to the sum of the discharge of water coming from the aquifer (Qai) and the discharge of leachate that is intercepted (Qdr). The value of Qai is important in the assessement of drain performance because infiltration of uncontaminated water increases the volume of fluid to be processed by the drainage system, therefore increasing operation costs.

On figure 7, the discharge ratios Qai/Qr, Qao/Qr, and Qdr/Qr are plotted along with the response curve for values of Hd/L of 0.75 and Ha/Hd of 1.10. Points A and C correspond to situations illustrated by the flownets of figure 6. Zone I of the response curve ($R/K < 0.03$) includes all situations where the flow field in the half cell is dominated by infiltration through the bottom boundary. Zone III ($R/K > 0.08$) includes situations where leachate is bypassing the drain with no infiltration from the bottom. Zone II ($0.03 < R/K < 0.08$) is the 'transition' zone where, at the bottom, flow occurs in both directions. From the relations between the different curves on figure 7, it can be seen that for:

zone I: Qa = Qai, Qao = 0

zone II: Qa = Qai + Qao

zone III: Qa = Qao, Qai = 0

Figure 8 shows the flow conditions occuring at point D of figure 7.

Optimization of the half cell system.

The efficiency of the leachate collection system will be highest when a maximum amount of leachate is intercepted and a minimum amount of water from depth is collected. For the response curve shown on figure 7, optimal drainage conditions will occur near point B.

It has to be understood that the conditions occuring at point C (and illustrated in figure 6c) are very unstable. Variations of any of the parameters due to transient effects could mean important changes in the flow conditions. Consequently, before concentrating efforts on developing an exact optimization procedure based on the half cell system, it is necessary to examine carefully the applicability of its assumptions to real-life situations. This is the object of present research for which preliminary work is described at the end of this paper.

COMPARISON BETWEEN LABORATORY AND NUMERICAL RESULTS.

The purpose of the laboratory experiments was to verify the results of the numerical model for simple hydrogeological conditions. The laboratory sand medium was originally assumed to be homogeneous and isotropic, with a hydraulic conductivity value of 4.18×10^{-3} cm/s. Figure 9 compares response curves from the laboratory and numerical models for values of Ha/Hd of 1.06 and Hd/L of 0.64. It can be seen that although the curves show the same trend, there is a significant difference in the values of the parameters. Three possible causes for the difference were considered: Numerical error, anisotropy in the laboratory sand medium, and error in the definition of the boundary conditions.

The best fit on figure 9 was produced using an anisotropy value (Kx/Ky) of 2. The elimination of the other possible causes lead us to believe that the difference in the laboratory and the numerical results was due to uneven packing of the laboratory porous medium which produced a slight anisotropy. The presence of inhomogeneities are also likely, and might be the cause behind the remaining difference between the curves of figure 9.

Although the results of the numerical model did not match perfectly the ones produced by the laboratory model, the good agreement between the trends of the two sets of results is sufficient to justify the use of the numerical model for more complex situations.

NON HOMOGENEOUS HALF CELL SYSTEMS

The effect of a layer of lower hydraulic conductivity on the half cell flow system was studied, with resulting flownets such as the one in figure 10. Figures 11, 12 and 13 show the effect of layer depth (d), thickness (b), and hydraulic conductivity contrast (K_1/K_2) on the response of the system. For the conditions tested in figure 11, the value of the response factor slightly increased with the depth of the layer for depths smaller than 4 m. If the layer was located deeper than 4 m, a change in depth did not affect the flow system.

Figure 12 shows the effect of layer thickness on the flow system. All other conditions remaining constant, an increase in layer thickness of up to 2 m. had a significant effect on the system. The decrease in Qa/Qr with an increase in thickness in the case where Ha/Hd = 1.15 was observed because the low permeability layer was preventing aquifer water from infiltrating into the system. The flow system was independent of layer thickness at values of thickness greater than 2 m. Figure 13 shows the effect of the conductivity contrast on the response factor. The hydraulic barrier effect produced by the low conductivity layer is reflected by the convergence of the response curves towards Qa/Qr = 0.

EFFECT OF DRAINAGE ON THE REGIONAL FLOW SYSTEM

In order to evaluate the conditions exterior to the half cell system, and to examine the effect of landfill drainage on a regional scale, flow systems such as the one shown on figure 14 are presently being studied. The system is homogeneous and lies on an impermeable base. It is recharged from the top at a constant, steady state flux of 20 cm/y. Recharge is also occurring through the left boundary (upflow) at a rate equal to the total recharge to the top that accumulates over a distance of 1000 m upstream from the left boundary. The hydraulic conductivity is equal to 0.1 cm/s. The right boundary is set at a constant head of 50 m. The water table position is found by iteration, and is plotted in exaggerated scale over the cross section. The length of the section is 1000 m and its thickness is 50 m. Drainage is represented by the introduction of a constant head node along the top boundary, 30 cm below the natural water-table. It is assumed that the pressure in the drain is zero and that the water table draws down to the drain. It can be seen on figure 14 that a component of horizontal flow exists in all of the streamlines leading to the drain section. The half cell system cannot be used to describe these drainage conditions because assumption 6 stating that no flow takes place across the side boundaries of the cell does not hold. Because the flow system of Figure 14 lies on an impermeable base, it represents an extreme case. If leakage was to occur down into a lower hydrogeological unit, a stronger vertical component of flow would appear.

Figure 15 shows equipotential lines for a system in which flow is mainly vertical. The bottom layer has the same boundary conditions as the system in figure 14. The ratio of hydraulic conductivities between the top and the bottom layer is 10^{-5}. Recharge to the top occurs at a steady state rate of 20 cm/y, and the lateral boundaries for the top layer are assumed to be impermeable. In this section, a groundwater divide exists on each side of the drain, and the potential at depth is nearly constant. Half cell assumptions 6 and 7 are valid and the half cell theory applies.

CONCLUSION

For landfills located on low permeability material overlying aquifers, the half cell approach might be a useful tool for the evaluation of leachate collection systems. Figure 15 shows how the zone located under the landfill can be divided into sections suitable for the application of the half cell model. In section A, symmetry boundaries exist under the drains and at mid-distance between them, thus defining the lateral limits of the half cell. Along the edge of the landfill, a symmetry boundary occurs between the vertical flow section (C) and the drain flow section (B), thus defining the limits of a second cell. The results of a sensitivity analysis presently under way will determine the type of conditions necessary for the situation described in figure 16 to occur. Work on a method to evaluate the drainage conditions in cases where horizontal flow occurs is also in progress.

ACKNOWLEDGEMENTS

The financial support from the Ontario Ministry of the Environment is gratefully acknowledged.

references

Abdul, A.S., St-Arnaud, L.C., Farvolden, R.N., Frind, E.O, Gillham ,R.W. (1985). Numerical modelling study of drain efficiency in leachate collection. Proceedings of the Ontario MOE Technology Transfer Conference No 6. p.396

Dematrocopoulis, A.C., Korfiatis, G.P., Bourodimos, E.L., Nawy, E.G. (1984). Modelling for design of landfill bottom liners, Journal of Environmental Engineering, Div. ASCE, Vol. 110, No. 6, p. 1084.

Farvolden, R.N., Carter, R.S, Abdul, A.S, Gillham, R.W. (1985). Laboratory study of tile drain efficiencies for leachate collection. Proceedings of the Ontario MOE Technology Transfer Conference No 6. ,p.369

Harr, M.E. (1962). Groundwater and Seepage, McGraw-Hill, New York, N.Y.

Kmet, P., Quinn, K.J., Slavic, C., (1981). Analysis of design parameters affecting the collection efficiency of clay lined landfills. Proceedings of the Fourth Annual Madison Conference of Applied Research and Practice on Municipal and Industrial Waste, held at the University of Wisconsin, Madison, Wisc, p.250

McBean, E.A., Poland, R., Rovers, F.A., Crutcher, A.J. (1982). Leachate collection design for contaminant landfills. Journal of Environmental Engineering Division, ASCE, Vol. 108, p. 204.

Moore, C.A., (1980). Landfill and surface impoundment performance evaluation manual U.S. EPA SW 869.

Wong, J. (1977). The design of a system for collecting leachate from a lined landfill site. Water Resources Research, Vol. 13, No. 2, page 404.

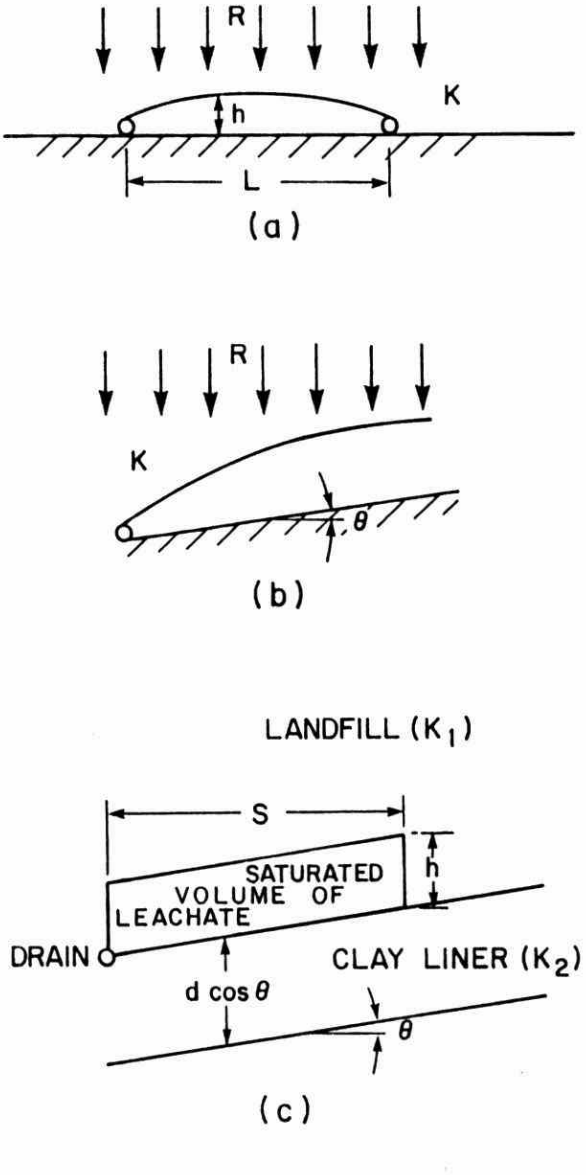


Figure 1. Three different leachate collection system geometries studied in the literature: (a) horizontal liner of zero permeability (Harr, 1962); (b) sloping liner of zero permeability (McBean et al., 1982); sloping liner of permeability K_2 overlain by a landfill of permeability K_1 (Wong, 1977).

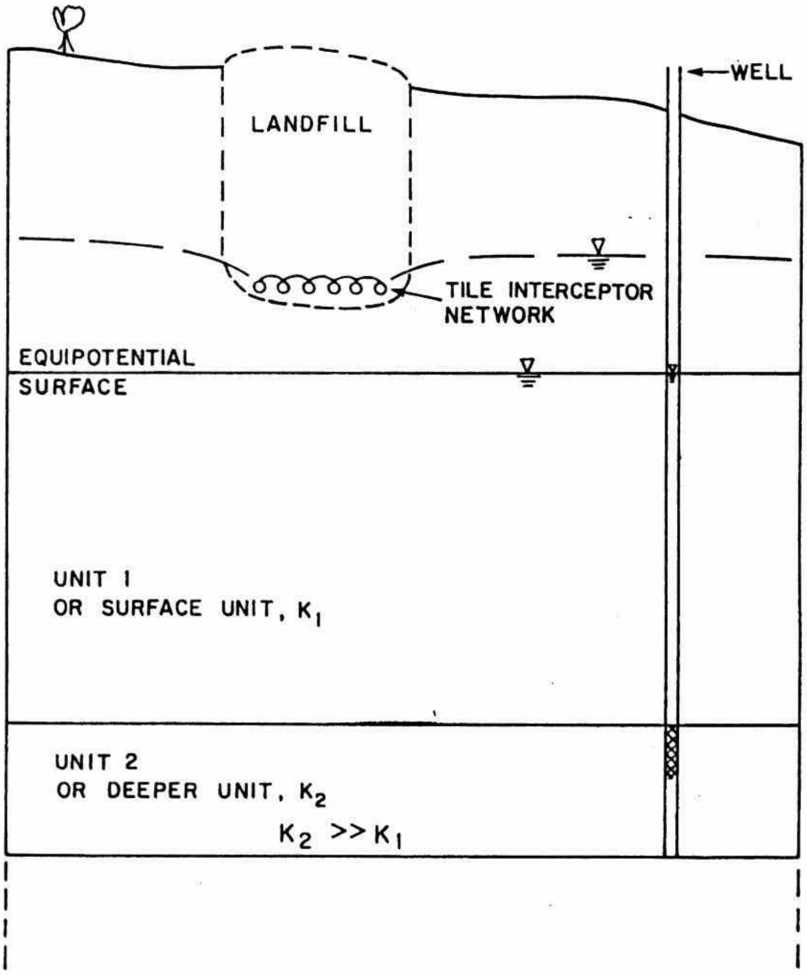


Figure 2. Schematic view of a landfill site.

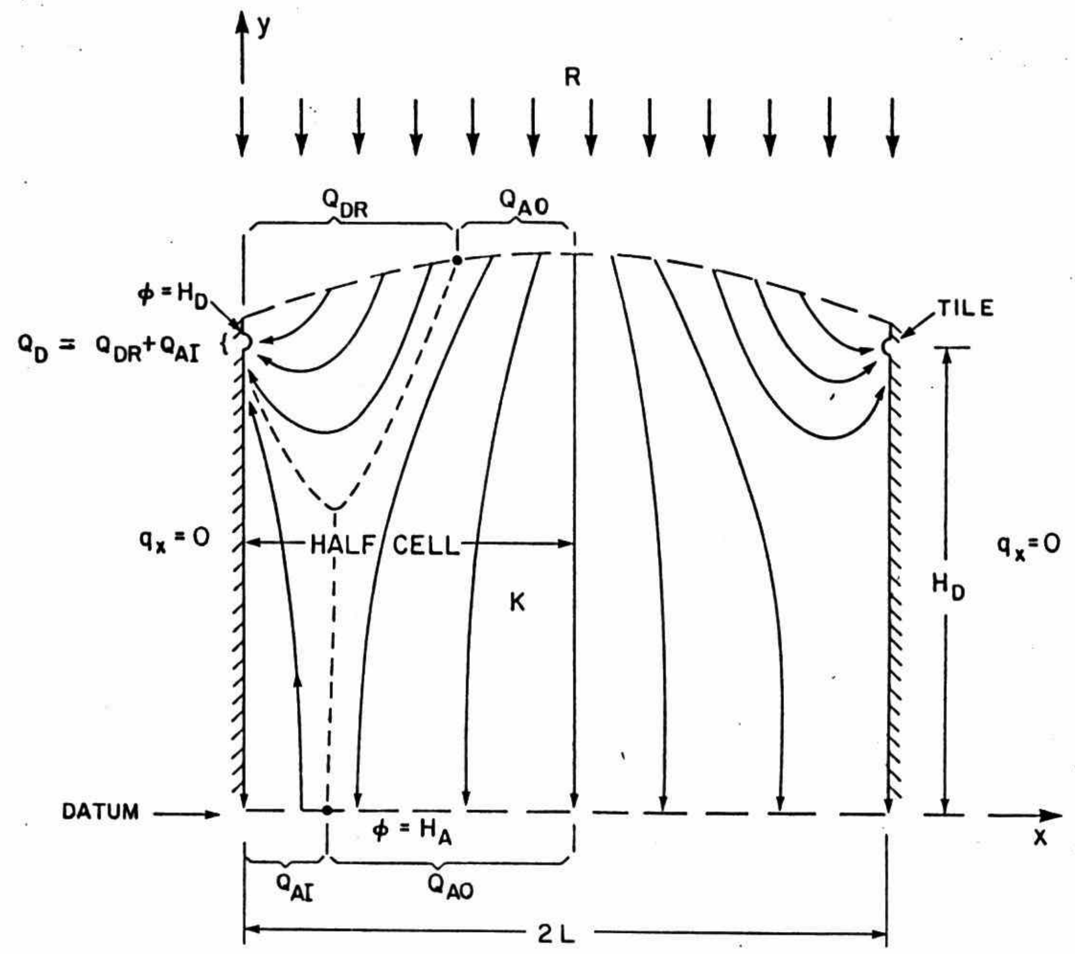


Figure 3. Drainage cell with boundary conditions and symbols.

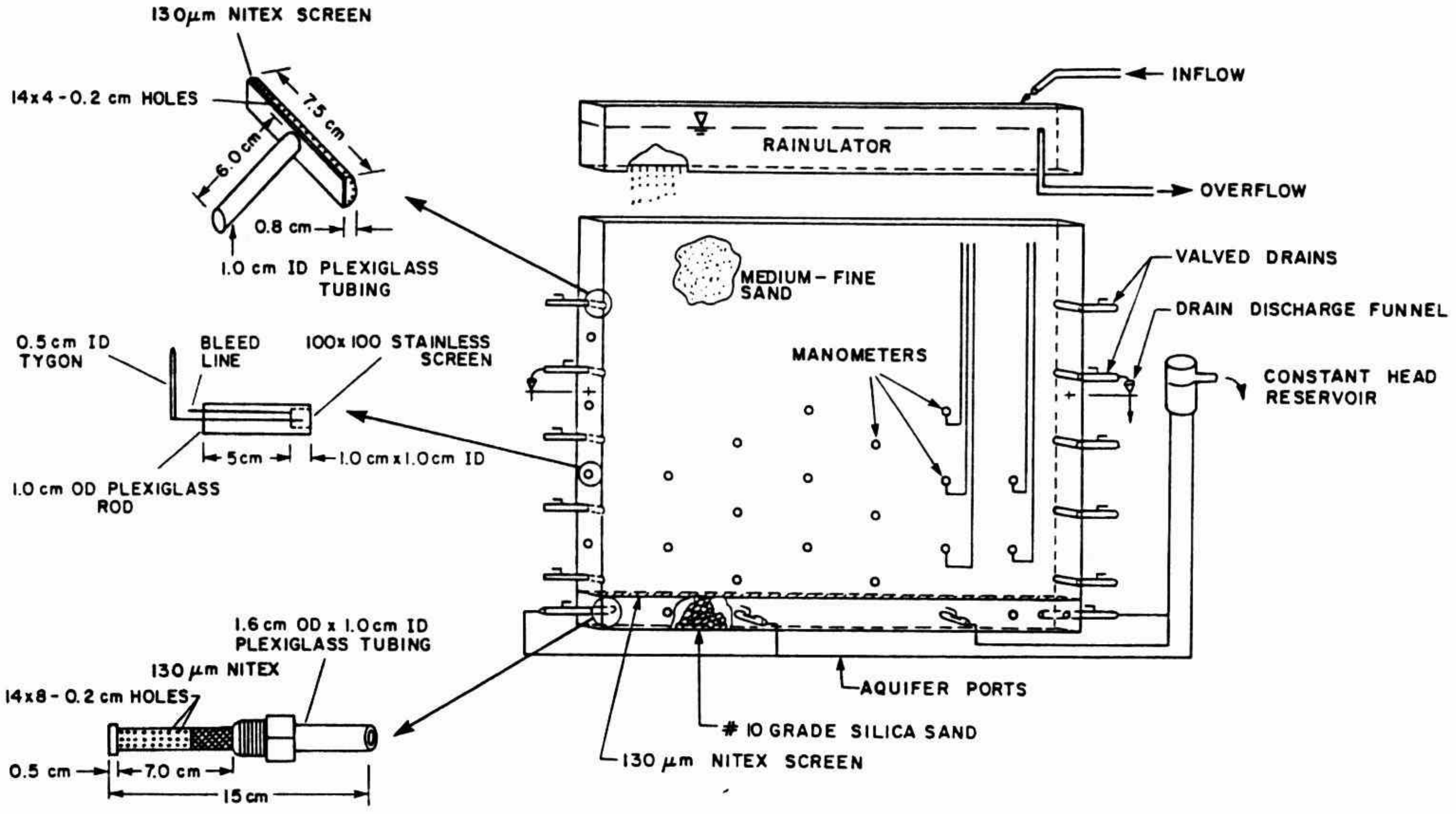


Figure 4. Experimental apparatus. The bottom layer of the box was packed with # 10 grade silica sand with a saturated hydraulic conductivity of 2.5 X 10^{-1} cm/s. The top layer was made of Chalk River medium fine-grained sand with a saturated hydraulic conductivity of 4.2 X 10^{-3} cm/s.

VARIABLE	*DESCRIPTION*	*UNITS*
Qr	Recharge of leachate	L^3/T
Qao	Discharge of fluid leaving system through bottom	L^3/T
Qai	Recharge due to fluid entering system through bottom	L^3/T
Qa	Resulting discharge at the bottom of the system (Qa=Qai+Qao)	L^3/T
Qd	Discharge of fluid leaving system through drain	L^3/T
Qdr	Discharge of leachate collected by the drain	L^3/T
Ha	Hydraulic head along the bottom of system.	L
Hd	Hydraulic head at drain.	L
L	Half spacing between drains.	L
R	Recharge flux.	L/T
K	Saturated hydraulic conductivity.	L/T
Qa/Qr	Response factor.	-
R/K	Hydraulic condition factor.	-
Ha/Hd	Induced head ratio.	-
Hd/L	Cell geometry factor.	-

Table 1. Description of variables and ratios used in the study.

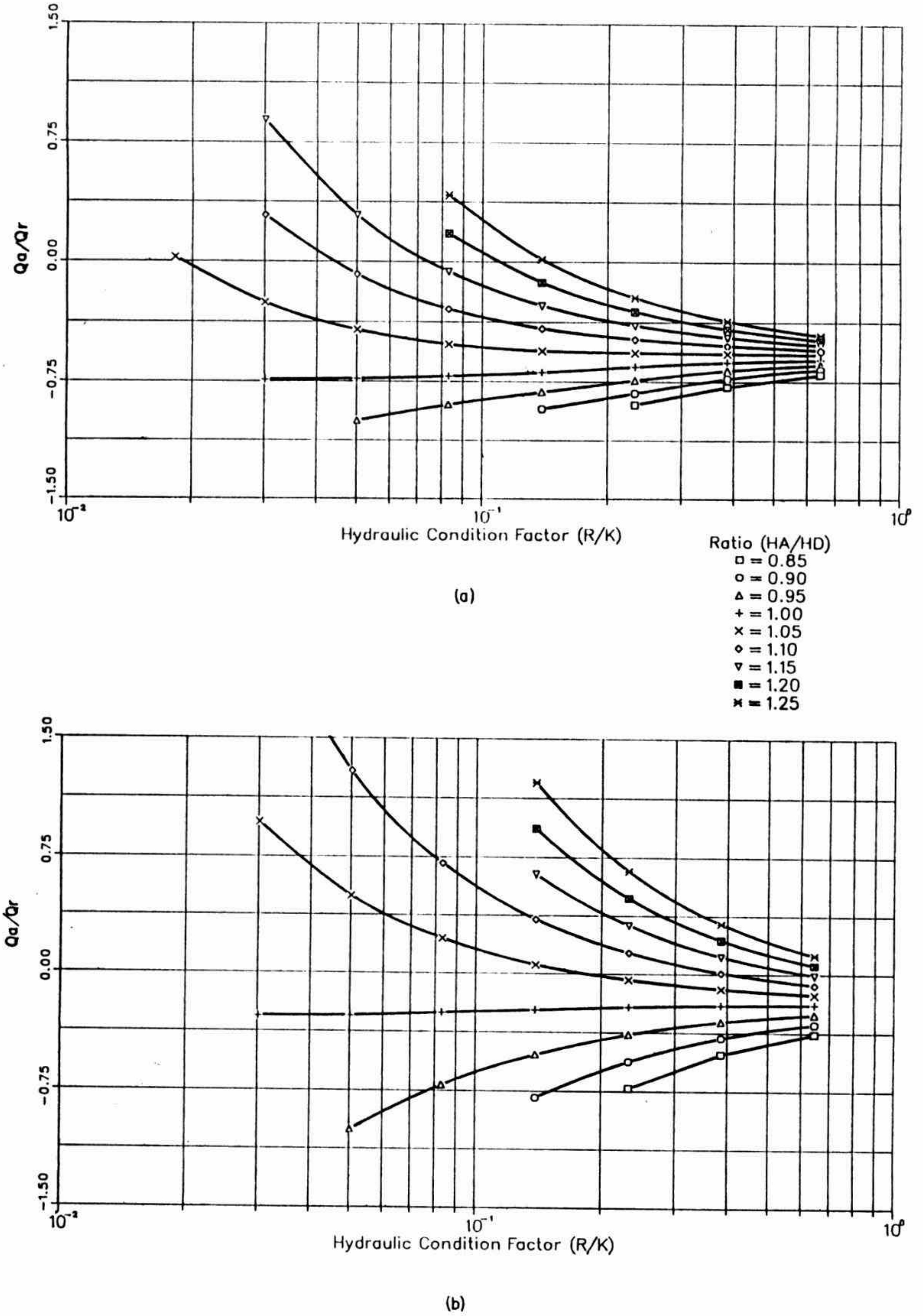


Figure 5. Response curves showing the relation between R/K and the response factor Qa/Qr. (a) Hd/L = 0.75, (b) Hd/L = 4.00. A comparison between the two sets of curves shows that collection is better as the drain spacing decreases.

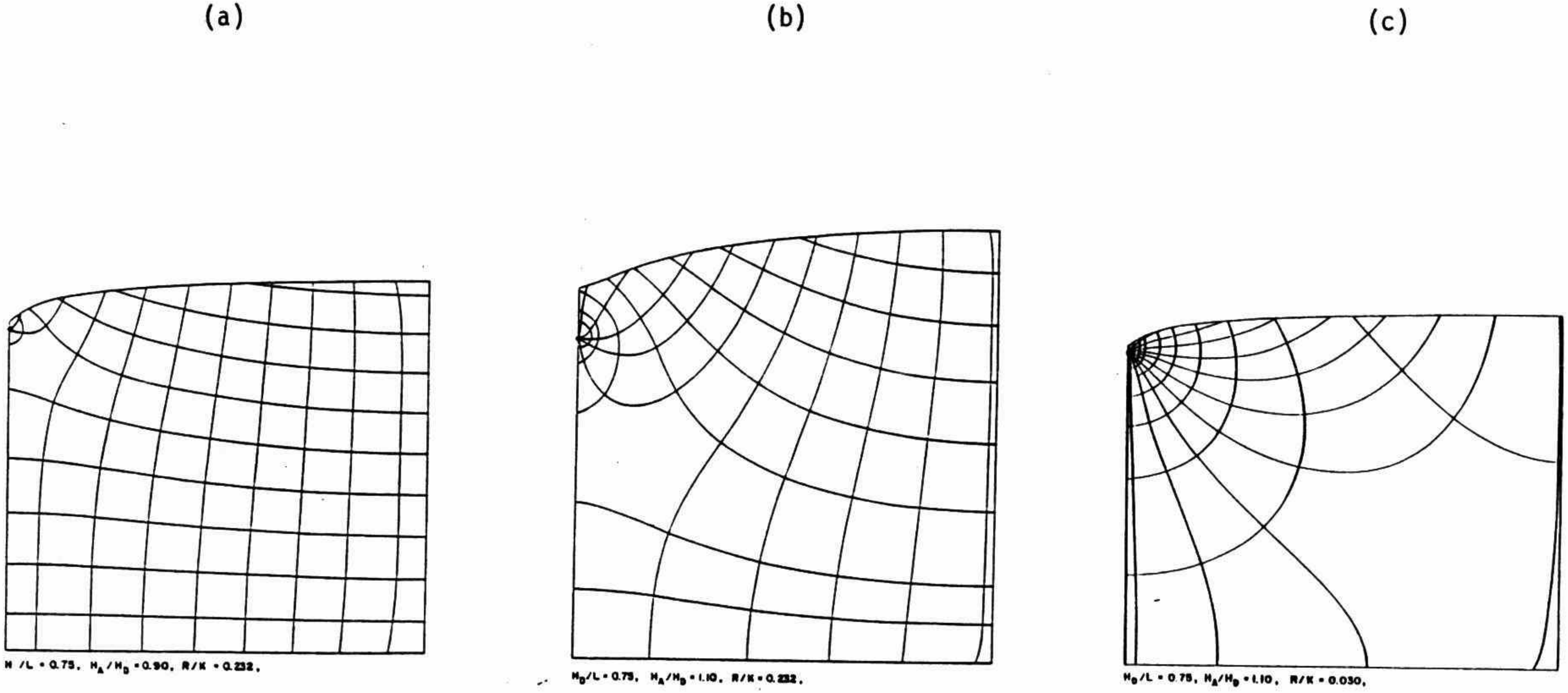

(a)
(b)
(c)
H /L = 0.75, H_A/H_D = 0.90, R/K = 0.232,
H_D/L = 0.75, H_A/H_D = 1.10, R/K = 0.232,
H_D/L = 0.75, H_A/H_D = 1.10, R/K = 0.030,

Figure 6. Flownets illustrating different flow conditions that may occur inside the half cell: (a) most of the leachate bypasses the drain, (b) approximately half of the leachate is collected, (c) all of the leachate is collected and infiltration from the bottom is occuring.

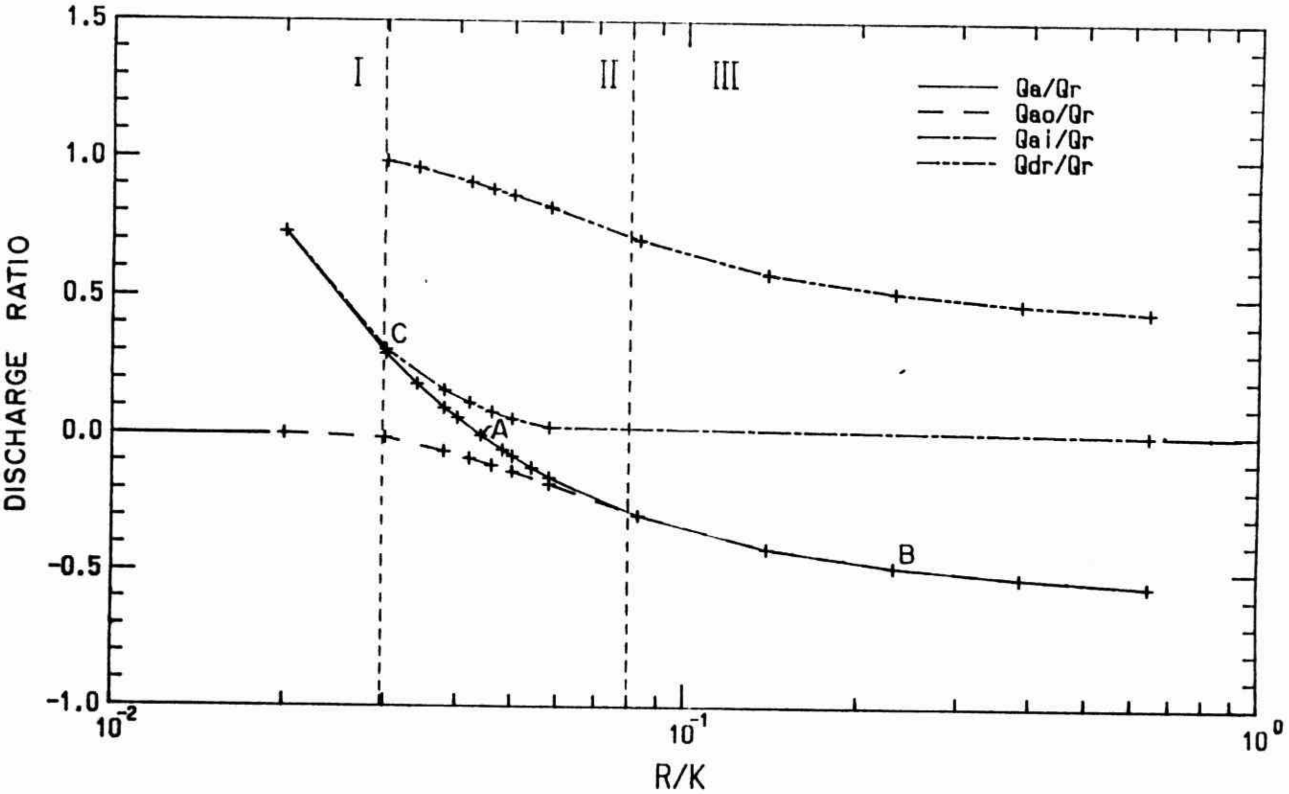


Figure 7. Response curve for conditions Hd/L = 0.75 and Ha/Hd = 1.10 (solid line) plotted along with the values of the other discharge ratios Qao/Qr, Qai/Qr and Qdr/Qr (dashed lines). Points B and C correspond to flownets 6b and 6c.

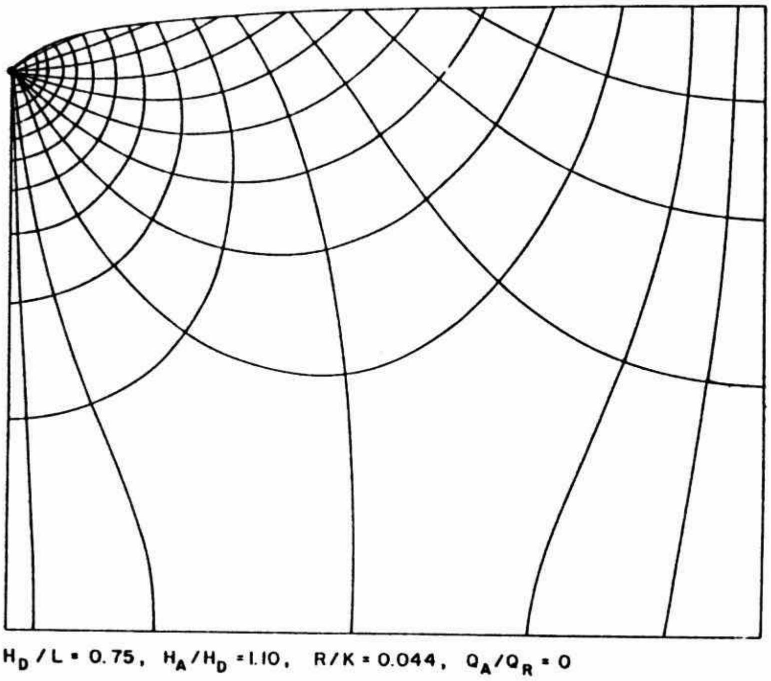

$H_D/L = 0.75$, $H_A/H_D = 1.10$, $R/K = 0.044$, $Q_A/Q_R = 0$

Figure 8. Flow conditions occuring at point A on figure 7.

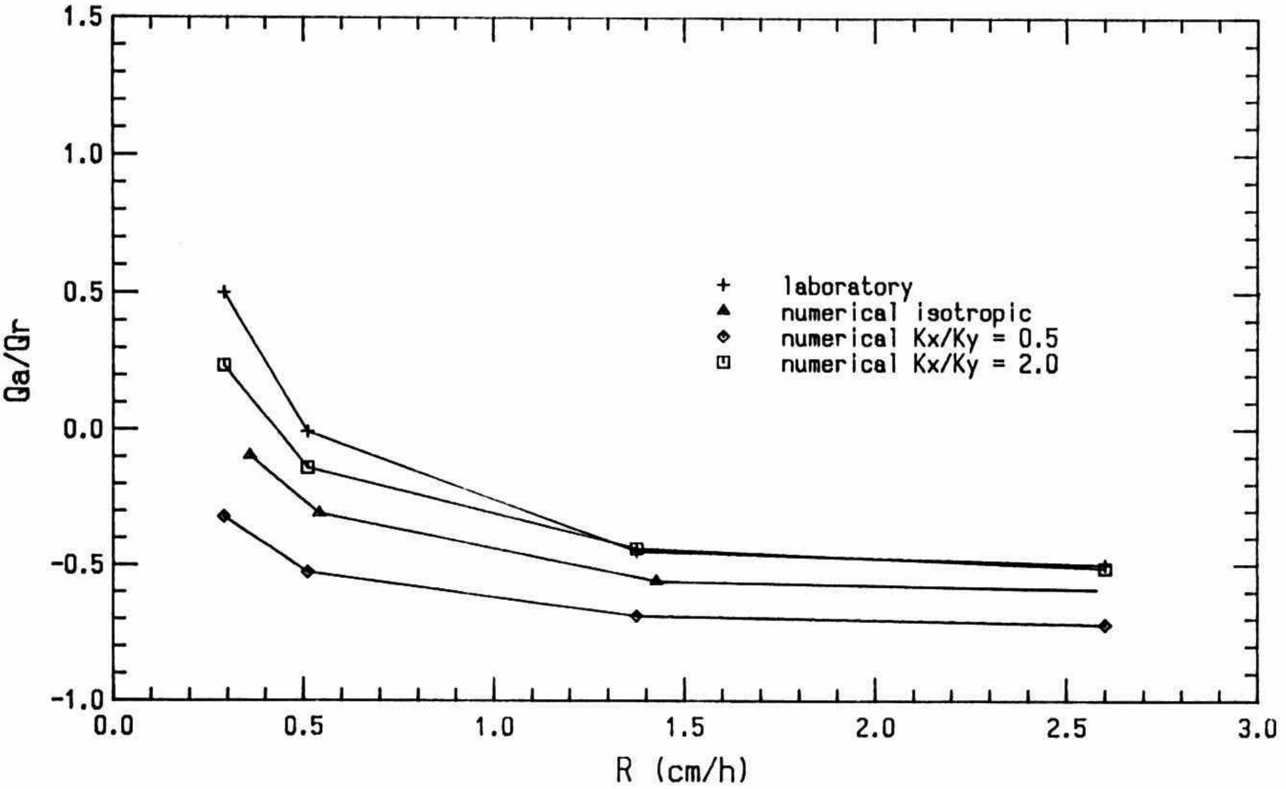


Figure 9. Laboratory and numerical response curves for Hd/L = 0.64 and Ha/Hd = 1.06. The value of Ky is constant at 4.2 X 10^{-3} cm/s.

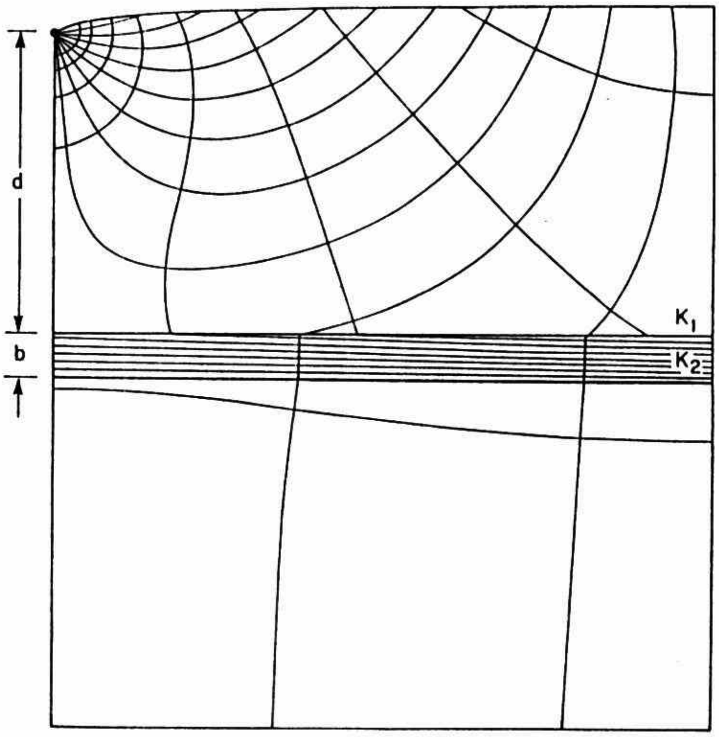


Figure 10. Half cell flow system including a low permeability layer.

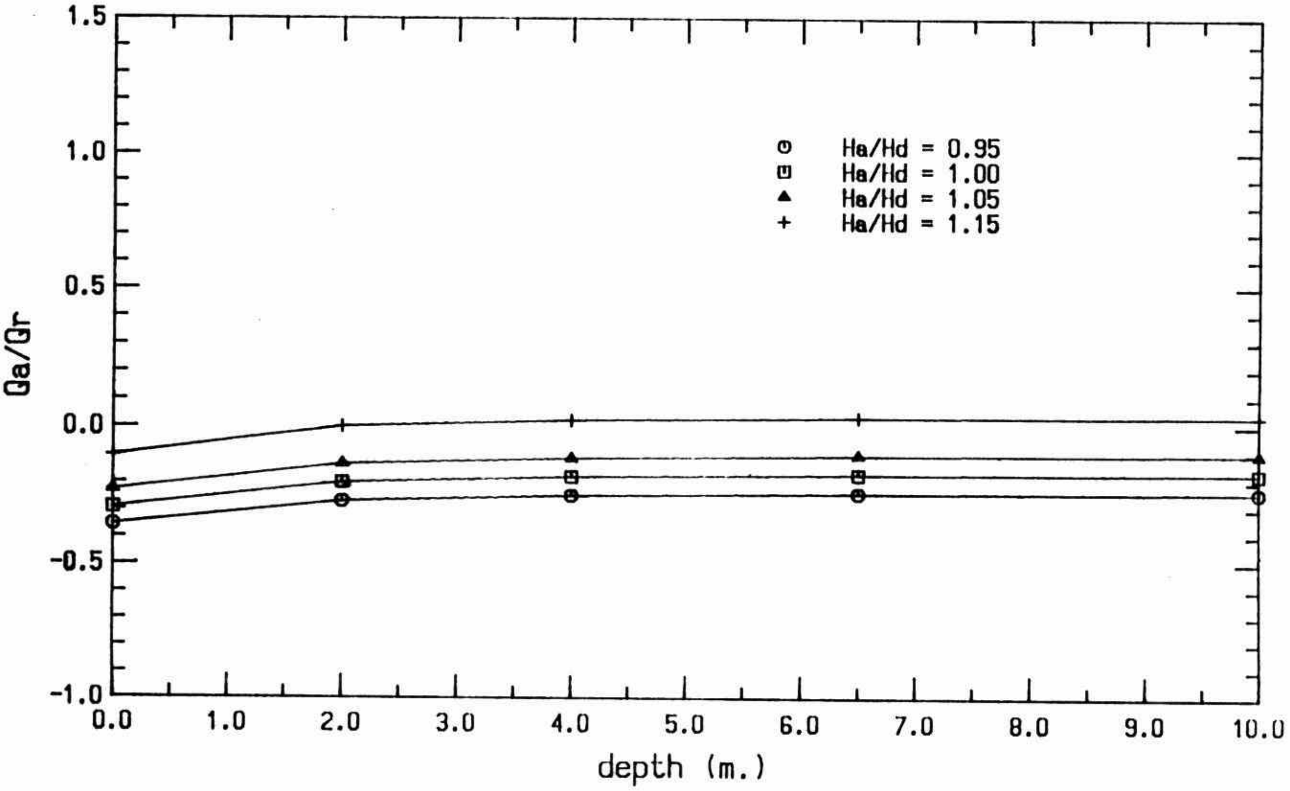


Figure 11. Response of the half cell system versus the depth of the low permeability layer for different values of Ha/Hd. Hd/L = 1.0 (Hd = 15 m, L = 15 m), $K_1/K_2 = 100.0$ ($K_1 = 1.2 \times 10^{-3}$ cm/s, $K_2 = 1.2 \times 10^{-5}$ cm/s), R = 9.6×10^{-5} cm/s., b = 1m.

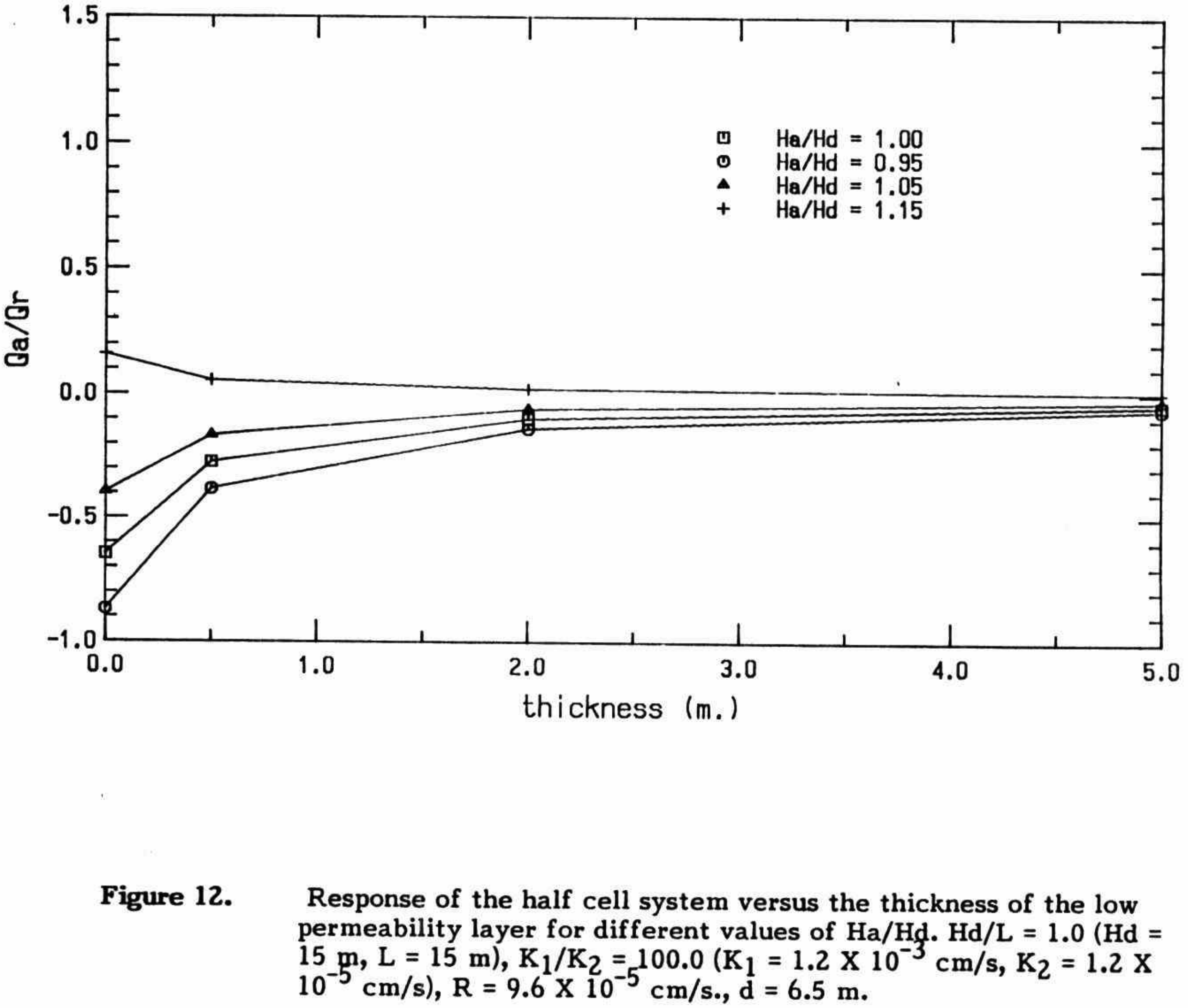


Figure 12. Response of the half cell system versus the thickness of the low permeability layer for different values of Ha/Hd. Hd/L = 1.0 (Hd = 15 m, L = 15 m), $K_1/K_2 = 100.0$ ($K_1 = 1.2 \times 10^{-3}$ cm/s, $K_2 = 1.2 \times 10^{-5}$ cm/s), $R = 9.6 \times 10^{-5}$ cm/s., d = 6.5 m.

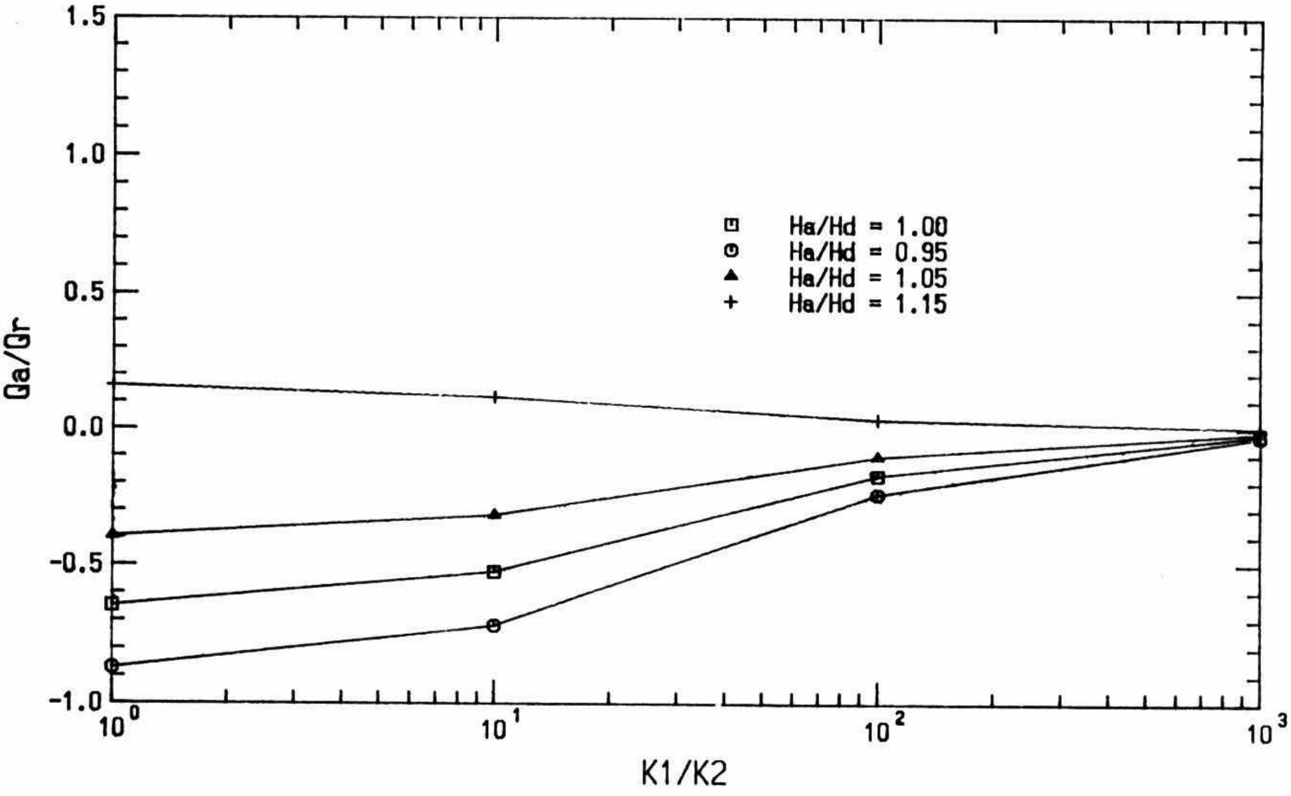


Figure 13. Response of the half cell system versus the hydraulic conductivity contrast between the low permeability layer and the rest of the cell for different values of Ha/Hd. Hd/L = 1.0 (Hd = 15 m, L = 15 m), $K_1 = 1.2 \times 10^{-3}$ cm/s, $R = 9.6 \times 10^{-5}$ cm/s., d = 6.5 m., b = 1.0 m.

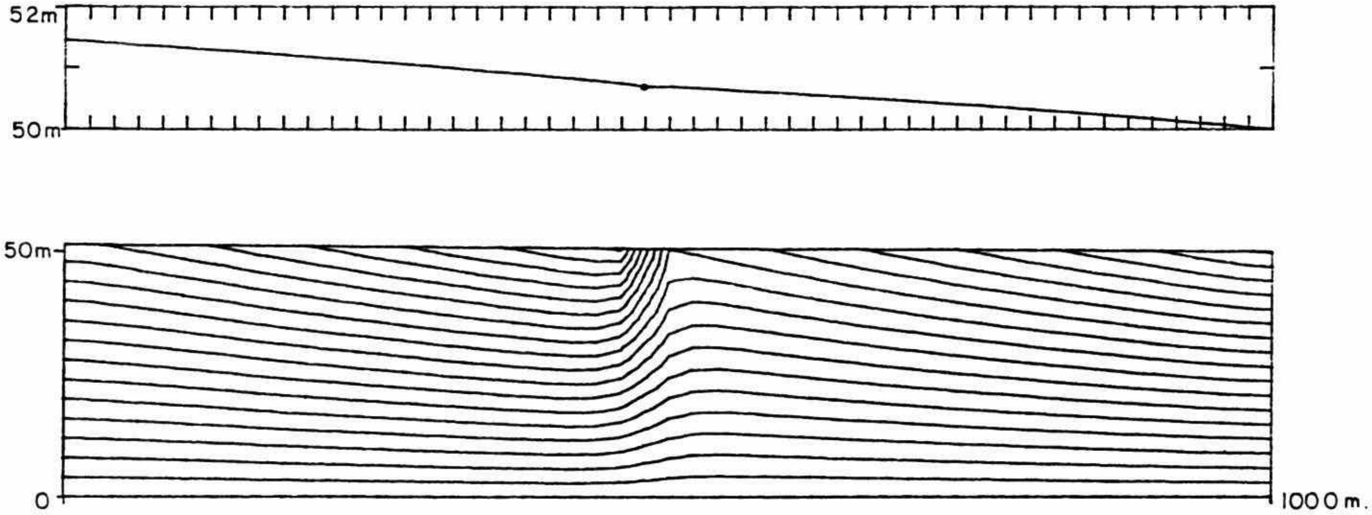


Figure 14. Flowlines describing drainage in a horizontal flow system.

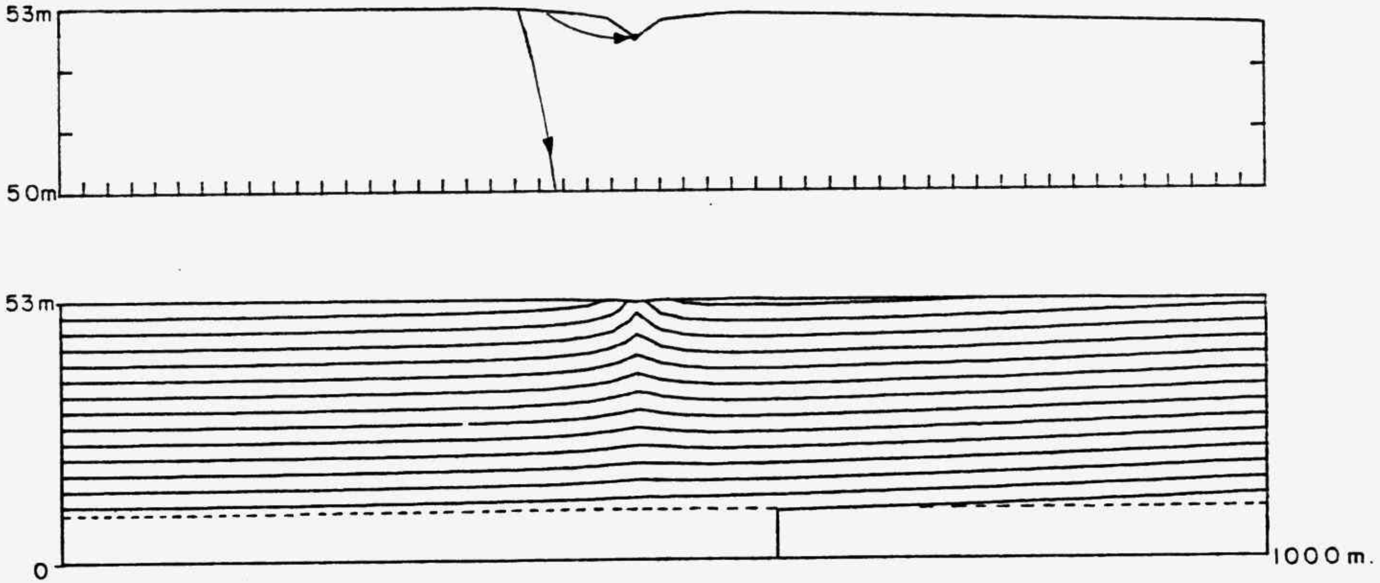


Figure 15. Equipotential lines for drainage in a vertical flow system.

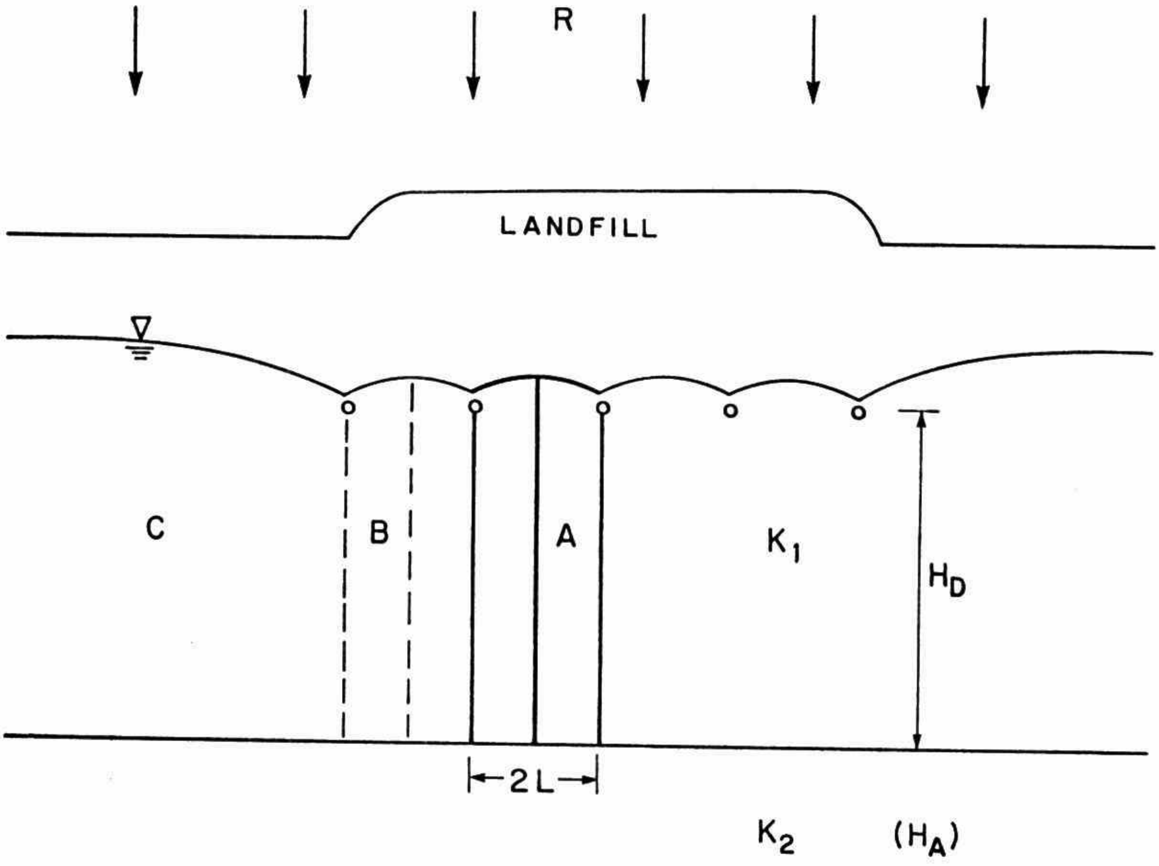


Figure 16. Groundwater flow zones under a landfill located in a low permeability hydrogeological unit.

AN INVESTIGATION INTO THE REDOX CONDITIONS OF A LANDFILL LEACHATE PLUME CONTAINING VOLATILE ORGANICS, GLOUCESTER, ONTARIO

By

L.C.M. Elliott and J.F. Devlin
Water and Earth Science Associates
Box 430, Carp, Ontario, K0A 1L0

Dr. F.A. Michel
Dept. of Geology
Carleton University, Ottawa, Ontario

Dr. W.A. Gorman
Dept. of Geological Sciences
Queen's University, Kingston, Ontario, K7L 3N6

Abstract

Recent research has indicated that the rate of degradation of organic compounds in ground water is dependent on the existing redox conditions. A detailed redox survey was carried out at the Gloucester Landfill site, Gloucester, Ontario, in 1985, to establish the redox conditions within a contaminant plume containing volatile organics. The redox conditions were characterised three ways: (1) EH measurements were made using a platinum electrode connected to a flow cell. PH and temperature probes were also connected to the flow cell so that all three field measurements could be recorded at the same time; (2) dissolved oxygen measurements were carried out with a second, independent, flow cell; (3) field and laboratory measurements of sulphate and sulphide concentrations in the ground water were carried out. These values were used to calculate a Nernstian "pe" for each sampling location. A concurrent study into the distribution of volatile organics on the site provided the contaminant data.

Redox conditions at the Gloucester site cannot be well defined by any single method. Measured Eh values were found to be imprecise and inaccurate, although general trends were evident in the data. Calculated Eh values could only be determined over a narrow range due to the analytical detection limits of the sulphide and sulphate analyses. Dissolved oxygen measurements do not reflect concentrations of other oxidized species which may affect the Eh.

Two transformations which may be occurring in the plume are trichloroethane to 1,1 dichloroethane, and toluene to carbon dioxide or methane. These processes appear to be proceeding very slowly.

Introduction

The Gloucester Landfill overlies an unconsolidated sedimentary sequence of interstratified sands, silts and gravels interpreted as littoral and sublittoral esker-fan deposits of the Champlain Sea (Rust and Romanelli, 1975). This sequence comprises two aquifer systems. A confined aquifer, approximately 20 m thick, overlying bedrock, is overlain by a silty clayey aquitard, 2-3 m thick, which is , in turn, overlain by the water table aquifer (about 6 m thick).

The landfill is located 2 km south of the Ottawa International Airport on the eastern flank of a northwest-southeast trending sand and gravel ridge which acts as a local ground water divide (Figure 1).

A detailed redox survey of the conditions within and around a contaminant plume in the unconfined aquifer at the Gloucester Landfill site was completed during the summer of 1985. Simultaneously, a separate study of the extent and distribution of volatile organic compounds within this leachate plume was also undertaken.

The purpose of this paper is to present the combined results of these studies in an effort to show the relationships between the redox conditions and the organic contaminant distribution within the leachate plume.

Site Hydrogeology

Recharge conditions prevail throughout the landfill west of the C.P.R. tracks (Gartner Lee, 1978). Vertical gradients between the shallow and confined aquifers gradually decrease eastward in the study area, reflecting the discharge conditions which prevail at the eastern end of the site.

The ground water flow direction was determined to be toward the east on the basis of water table elevation data collected using an electric sonde.

The hydraulic conductivity of the aquifer material was determined by Hvorslev's method for single piezometer slug tests (Freeze & Cherry, 1979). Results indicate that K ranges between 5.9×10^{-6} and 5.1×10^{-5} m/s.

Estimates of the ground water velocity range from <1 cm/day to 14 cm/day on the basis of point dilution measurements and hydraulic gradients.

Field Methods

Fifteen piezometers and twenty-two multilevel samplers were monitored at the northeast plume site (Figure 2). Measurements of pH, Eh and temperature were conducted in an air-tight flow cell using a mercury thermometer and combination pH and platinum electrodes (from Orion Research Inc.) connected to a battery powered Metrohm pH/mV/T meter. The flow cell was flushed at approximately 100 ml/min for a minimum of 10 minutes with the sample prior to taking meter readings. Between each sample measurement the pH and redox electrodes were calibrated; the pH electrode in buffer solutions of pH 4, 7 and 10, and the redox electrode in a poised solution of ferrous ammonium sulphate, ferric ammonium sulphate and sulfuric acid with a redox potential of +475 mV (Light, 1972).

Dissolved oxygen concentrations and temperature were measured using an Orbisphere Dissolved Oxygen Meter (model #2713). Calibration was carried out at the beginning of each day by zeroing the meter reading with the sensor immersed in a 10% by weight sodium sulfite solution. The sensor was stored in this anaerobic solution when not in use.

Sulphide measurements were made in the field using a portable HACH DREL 2 Spectrophotometer with range expander. The HACH Methylene Blue method was used for the determination of total sulphide.

The spectrophotometer was calibrated at each multilevel sampling location using daily prepared fresh sulphide standards. These precautions ensured that: (1) fluctuations in the power source which caused changes in the calibration curve were compensated for; and (2) the calibration curves were not affected by the rapid decay of sulphide standards.

Samples for sulphate analysis were collected in glass vials immediately following the sulphide analyses and transported to the National Hydrology Research Institute laboratory at the end of the day. All samples were refrigerated at 8°C until analysed.

Samples for the analysis of volatile organic compounds were collected using a peristaltic pump and stored in polypropylene syringes. The collection system, developed by Farrington Lockwood Co. Ltd. (1983), permits the collection and analysis of the samples to occur without ever exposing them to the atmosphere. All parts of the sampling equipment that come into direct contact with the water being sampled were transported to and from the field in sealed plastic bags inside a tightly sealed cooler; this measure prevented exposure to, and contamination from, gasoline fumes.

Analytical Methods

Sulphate analyses were performed on the HACH DREL 2 Spectrophotometer using the HACH turbidimetric method. All sulphate samples were analysed within 10 days of sampling.

Analyses for weak organic acids were carried out using a Dionex System 12 Analyser in the Ion Chromatography Exclusion Mode (I.C.E.). Acetate and chloride analyses were also performed by standard Ion Chromatography.

Volatile organic compounds were analysed using a Spectra-physics Model 7100 Gas Chromatograph equipped with an Envirochem Unacon 810 purge and trap unit. Samples (15 mLs) were purged 12 minutes with high purity helium gas. Separation of the compounds was achieved with a 0.25 mm diameter wall coated open tubular capillary column. The system was equipped with both F.I.D. and Hall detectors.

Results

Nernstian Eh values were calculated on the basis of the $SO_4^{=}/HS^{-}$ couple using the following equations from Stumm and Morgan, (1981).

$$pE = 4.25 - 1.125\ pH + 0.125\ pSO_4^{=} - 0.125\ pHS- \qquad (1)$$

$$Eh = 0.059\ pE \qquad (2)$$

In order to obtain representative values of HS^- from total sulphide measurements for the above calculation, it was necessary to assume equilibrium conditions and that;

$$\text{total sulphide} = H2S + HS^{-} + S^{2-} \qquad (3)$$

The range of Eh values determined using equations (1) and (2) is only -150 mv to -300 mv. In general, the lowest values correspond to measurements taken from the bottom of the unconfined aquifer. However, in a few locations low Eh´s were determined in near surface ground water (99PM, 107M, 108M). In these instances it is thought that local conditions, such as those produced by buried vegetation, are responsible for the sulfur content of the water, and hence the apparently low Eh.

Eh values, measured using the platinum electrode, range from about 0 mv to 550 mv. In general, the highest values correspond to shallow locations (ie. at depths of about 2 m). There is some suggestion in the data that the shallow ground water at the site is increasingly oxidizing toward the east. In the deeper ground water, the lowest Eh values occur in the areas of greatest organic contamination.

Dissolved oxygen concentrations range between 4 ppm and <0.1 ppm (100 ppb). The highest concentrations were measured in the very shallow regions of the aquifer. The concentrations dropped off rapidly to values of less than 150 ppb for most of the aquifer thickness.

Significant noise was encountered when oxygen concentrations fell below 100 ppb (+/- 15%). Oxygen, entering the flow cell through the polyethylene and silicone tubing of the monitor and the pump, may account for this background noise (Orbisphere Laboratories).

Volatile Organic Contamination

Twenty volatile organic compounds have been identified in the ground water at the northeast plume site by G.C./M.S. Of these, 1,2 dichloroethane (12DCEA), benzene, trichloroethylene (TCEY), toluene, and chlorobenzene (ClBENZ) have been studied quantitatively. Tetrahydrofuran (THF) and diethyl ether (DEE) have been tentatively identified by G.C. and also studied quantitatively, but their presence has not been confirmed by M.S. A detailed description of the distributions of all these compounds can be found elsewhere (Devlin and Gorman, in press). For the purposes of this discussion, the distributions of benzene and toluene are described and are typical of the distributions of the other volatile organic contaminants (Figures 2 and 3).

The source of the organic contamination seems to be located west of the study site. The plume appears to be migrating along a very narrow path between 99M and 100PM (25 m wide) and extends east beyond 118M. However, the lack of lateral control east of 112M restricts a firm definition of the plume width to the western and central portions of the study area. Both toluene and benzene show two concentration maxima: a well defined maximum between 109M and 113M, and a poorly defined maximum beginning near 118M and extending east. In section, the contaminants appear to be following two flow paths: in the western portion of the study area, low levels of toluene (not shown in Figure 3) occur at a depth of about 4-5 m while the remaining chemicals are most concentrated at depths of 6-7 m. East of 109M, the plume appears to be migrating at about 5 m depth. This pattern continues until 115M and 117M where the concentration maxima are once again at 6 - 7 m depth.

DISCUSSION

The three methods used to investigate the redox conditions at the study site are, ideally, examining different manifestations of the same process. Thus, in the ideal case one might expect perfect correlations between:

(1) Eh (measured) and Eh (calculated).
(2) Eh and dissolved O_2 concentration.

However, when these parameters are plotted against one another the correlations are weak (Figures 4 and 5). This indicates that ideal conditions do not exist at the study site, and in order to interpret the data close attention must be paid to exactly what is being measured by each method.

Considerable research has been carried out to determine the relationship between Eh values measured using a platinum electrode and those predicted by thermodynamics (Baas Becking et al., 1960; Garrels and Christ, 1965; Stumm and Morgan, 1981; Jackson and Patterson, 1982). The electrode measures an exchange current produced during the course of oxidation reduction reactions. "Slow" electrodes, where there is a large change in electrode potential required to induce a measurable exchange current, and "mixed" potentials, in which several redox processes may be involved in the apparent "equilibrium" potential, have been cited as causes of imprecise and inaccurate Eh measurements, respectively (Stumm and Morgan, 1981).

Jackson and Patterson (1982) found that field measurements of Eh using a platinum electrode were consistently higher than Eh values determined indirectly using analytical information ($H_2S/SO_4^=$). A similar trend has been observed in the data from the Gloucester site. There are two possible causes for the observed discrepancy in values: (1) the measured potentials are actually "mixed" potentials, and do not accurately reflect the equilibrium Eh values; (2) the assumption of equilibrium, which is implicit in the indirect evaluation of Eh, is unjustified. The former cause was considered to be the most likely one by Jackson and Patterson (1982). It should be noted that although the measured Eh values may be inaccurate in a quantitative sense, they may still be useful in a qualitative analysis. For example, oxidizing solutions will exhibit higher Eh´s than reducing solutions.

Although the indirect method of determining Eh values may provide more accurate data, there are limitations to the procedure. To begin with, as noted above, the system under study must be in equilibrium. Secondly, both members of the couple must be present at concentrations which are measurable. This constraint severely limits the range of Eh values which can be determined using any one couple (Cherry et al., 1979). For example, when the $H_2S/SO_4^=$ couple is used to determine Eh values, a 10,000 fold change in the relative concentrations of the two members only corresponds to a 30 mV difference in the calculated Eh´s (Table 1). So, at a site where there is a wide variation in Eh conditions, a single redox couple will be insufficient to define all those conditions.

Table 1: Calculated Eh values for various concentrations of H_2S and $SO_4^=$.

Concentrations				Eh (calc.)
H_2S		$SO_4^=$		(mv)
ug/L	moles/L	mg/L	moles/L	
5	1.47×10^{-7}	200	2.08×10^{-3}	-183
50	1.47×10^{-6}	20	2.08×10^{-4}	-198
500	1.47×10^{-5}	2	2.08×10^{-5}	-212

calculations were performed assuming a pH of 7.

Water saturated with air has an oxygen content of about 8 ppm at 20°C. But at what concentrations of oxygen are waters considered to be "anoxic"? Stumm and Morgan (1981) have used the term "anoxic" to describe systems in which the supply of dissolved oxygen is depleted to the extent that the primary oxidizing agent is nitrate (or another lesser oxidized species). Such a system could have a theoretical Eh of more than 300 mv (Stumm and Morgan, 1981, pp. 459). Thus, it is possible for a solution low in dissolved oxygen to exhibit a relatively high Eh. This seems to be the case in some locations at the Gloucester site (Figure 5).

It can be seen from the above that dissolved oxygen measurements cannot, by themselves, define the redox environment of a site. However, oxygen is involved in many biologically mediated reactions and a direct measurement of its availability to organisms can be invaluable in predicting the transformation products of contaminants in ground water.

The data which were collected using the three methods have been combined to produce a cross-sectional view of the redox zones within the northeast plume (Figure 6). The map was prepared in two steps: Firstly, an oxygen availability index was calculated based on the $H_2S/SO_4^=$ equilibrium,

$$H_2S_{(aq)} + 2O_{2\,(aq)} = SO_4^{\,2-}{}_{(aq)} + 2H^+_{(aq)} \quad K = 1.35 \qquad (4)$$

(K calculated using thermodynamic data from Stumm and Morgan, 1981)

Analytically determined values for pH, sulphate concentration and total sulphide concentration at each monitoring location were inserted into equation (5) to derive a theoretical equilibrium dissolved oxygen concentration.

$$\text{ppb } O_2 = 32 \times 10^6 \sqrt{\frac{(10)^{-2pH} \; (\text{ppm } SO_4^= /96000)}{1.35 \; (\text{ppb } H_2S/34 \times 10^6)}} \qquad (5)$$

where,

ppb O_2 = dissolved oxygen concentration in ppb
ppm $SO_4^=$ = sulphate concentration in ppm
ppb H_2S = total sulphide concentration in ppb

The oxygen availability index is defined as a ratio between the theoretical dissolved oxygen concentration and the measured concentration (equation 6).

$$\text{OAI} = \text{ppb } O_2 \text{ (measured)/ ppb } O_2 \text{ (theoretical)} \qquad (6)$$

An index value significantly greater than unity indicates a surplus of available oxygen, while a value less than unity indicates an oxygen depletion. Both these cases also suggest a disequilibrium in the $H_2S/SO_4^=$ redox couple. Values near unity indicate there is equilibrium between the oxygen and sulfur species. In this case, O_2 may or may not be available to react with organic material, depending on the concentrations of other oxidized species.

In the second step of the cross-section preparation, the index values were matched to their corresponding Eh (measured, Pt electrode) values and three zones were defined:

(1) An oxygenated zone in which the OAI>10 and Eh (meas.) is >100 mv.

(2) A transition zone in which 1<OAI<10 or Eh (meas.) is <100 mv or both conditions exist.

(3) A reducing zone in which OAI<1 and Eh (meas.)<100 mv.

The cross-section (Figure 6) shows that the most reducing zones are located at the west side of the study site, near the former disposal trenches, and in the central portion of the site. The transitional zone stretches across the whole site, but appears to be tapering off in the direction of the front of the plume.

Volatile Organics

The relationship between the redox environment and the contamination at the Gloucester Site is clearly evident in Figures 7 and 8. The highest levels of contamination exist in relatively reducing environments. This is true for both aromatic and polyhalogenated contaminants.

The relationship between Eh and chloride is notably less pronounced than that between Eh and the organics (Figure 9). This indicates that the trend evident in Figures 7 and 8 is not merely a function of the flow path of the plume i.e. not all contaminants occur exclusively within the reducing environment of the plume.

There are two explanations for the observed trend:

(1) The organic contaminants in the oxidizing zones of the aquifer have been transformed and are no longer detectable while those in the reducing zones persist due to slow reaction rates. By this reasoning it is the redox environment which determines the apparent distribution of the organics.

(2) The dissolved oxygen (and other oxidized species) is depleted in the zones of severe organic contamination by the oxidation of the contaminants. By this reasoning it is the presence of organics which determines the redox zonation within the aquifer.

Both of the above mechanisms are probably at work at the Gloucester site. Previous research carried out at landfills has indicated that reducing conditions are often encountered in the immediate vicinity of the buried refuse (Baedecker and Back, 1979(a); Nicholson _et al._, 1982; Hoeks and Borst, 1981). Figure 6 shows that there is a strongly reducing zone located at the west end of the study site near the original disposal trenches. It is possible that this zone was already established when the volatile organics were disposed.

There is also evidence for the second mechanism. According to Figure 6, there is a second reducing zone located at a depth of about 3m at monitor 112M. This zone corresponds in position with the maximum concentrations of benzene and toluene (Figures 2 and 3). Wilson _et al._ (1986) showed that these compounds can be anaerobically transformed to CO_2. Such a process would be expected to deplete the concentrations of oxidized species, resulting in a reducing zone.

Transformations

The relationship between the redox environment and the fate of various organic compounds has been the subject of much recent research. Reviews of this work have agreed that there is growing evidence that aromatic compounds are most quickly degraded under oxidizing conditions, while most halogenated aliphatic compounds are degraded only under reducing conditions (Jackson et al., 1985; Mackay and Vogel, 1985; Wilson et al., 1986). At the Gloucester site, the organic contamination is restricted to the transitional and reducing zones of the plume. Therefore, this discussion will focus on the anaerobic transformations which might be taking place.

Volatile Fatty Acids

Farquhar and Rovers (1973) reported that complex organic compounds may be fermented anaerobically yielding soluble organic acids which are subsequently transformed to methane and carbon dioxide.

The only identifiable organic acid at the Gloucester site was acetic acid. This substance was only detectable in the zones of severe organic contamination where reducing conditions prevailed. There, it reached concentrations exceeding 1000 mg/L.

The origin of the acetate is unclear. A number of sources have indicated that acetate can be quickly biotransformed in the subsurface (i.e. on the order of weeks) (Hoeks and Borst, 1981; Roberts et al., 1980). Since the contamination has been estimated to be at least 9 years old at the time of sampling (Devlin and Gorman, in press), the continued presence of high concentrations of acetate may be an indication that biological activity at the site is low, and that most of the acetate present was codisposed with the volatile organic wastes.

Halogenated Aliphatics

According to Mackay and Vogel,(1985) the two major chemical reactions for halogenated aliphatics in aqueous solution are hydrolysis (substitution), which leads to the removal of a halogen atom and the formation of an alcohol, and elimination, which leads to the removal of a halogen atom and the formation of an alkene. In addition to these processes, halogenated aliphatics may undergo biologically-mediated transformations which result in the removal of halogen atoms. Parsons and Lage (1985) reported the transformation of TCEA to DCEA; Wilson et al. (1986) reported the transformation of TCEY to 12DCEA and ultimately to vinyl chloride.

A possible result of the transformation process is that compounds are produced which are more mobile than the original wastes. This is particularly true with halogenated aliphatics undergoing dehalogenation reactions. However, previous work has indicated that the differences in contaminant mobility at the northeast plume site are small due to the low organic carbon content of the sediments (Devlin and Gorman, in press). Thus, it would be expected that parent-daughter compounds would be detected together wherever the reactions have begun.

At the study site, three pairs of compounds have been identified which could be related by the transformations described above:

(1)	111TCEA	--->	11DCEE	Elimination
(2)	111TCEA	--->	11DCEA	Dehalogenation
(3)	TCEY	--->	11DCEE	Dehalogenation

The distributions of these compounds through the centre of the contaminant plume have been plotted in Figures 10 and 11. Only the second pair of compounds are present in a distribution which is consistent with a parent-daughter relationship. This transformation appears to be occurring in the reducing zone at monitor 112M.

Aromatics

Among the aromatic compounds detected at the study site, benzene and toluene are the most widely distributed (Figures 2 and 3). Aromatics are most quickly biodegraded in an aerobic environment, however, as mentioned previously, anaerobic degradation to CO_2 has also been shown to occur (Wilson et al., 1986). These processes would be expected to deplete the concentrations of oxidized species, resulting in a locally reducing environment.

The maximum concentrations of toluene and benzene occur between monitors 110M and 113M (centering on 112M) where a strongly reducing zone has been defined. Additional maxima have been found at the eastern edge of the site where Eh measurements and dissolved oxygen concentrations indicate that the conditions are transitional to reducing. The concentrations of sulfur species were below the analytical detection limits in this area, so the OAI values could not be calculated.

Although the locations of the concentration maxima are similar for benzene and toluene, the overall distributions of the contaminants differ. Toluene appears to be less diffuse than benzene. This difference could be the result of the more rapid biodegradation of toluene. Wilson et al. (1986) reported that toluene was the only alkylbenzene which did not require a lag time before being anaerobically degraded (other compounds tested included benzene, ethylbenzene and xylenes). Work performed by Water and Earth Science Associates on a gasoline spill, in Eastern Ontario, has shown that toluene is rapidly attenuated while benzene is detectable over the entire length of the plume.

Conclusions

The redox conditions at the Gloucester Landfill site cannot be well defined by a single method. Eh´s measured with a platinum electrode are useful as a qualitative tool to distinguish oxidizing and reducing zones, however, the measurements may be imprecise, due to "slow" electrode response, and they may be inaccurate due to "mixed" potentials in the ground water.

Eh´s determined from analytical data may accurately reflect the conditions of the ground water, however, it is only possible to calculate values within a narrow Eh range. Beyond this range, the members of the redox couple are not analytically detectable.

Dissolved oxygen measurements provide information about the availability of oxygen but not about the availability of other oxidized species which could influence the solution Eh.

Organic contaminants at the site were found to exist only within the more reducing portions of the aquifer. This is probably due to slow reaction rates within existing reducing zones, and transformations which have depleted the concentrations of oxidized species within the aquifer.

Two possible transformations have been identified in the leachate plume: trichloroethane to 1,1 dichloroethane and toluene to CO_2 or CH_4. Both of these processes are taking place near the most reducing portion of the plume. The high concentrations of acetate detected in this area suggest that any biologically mediated transformations are proceeding very slowly.

References

Baas Becking, L.G.M., Kaplan, I.R., Moore, D.
1960: "Limits of the Natural Environment in Terms of pH and Oxidation Reduction Potentials", J. Geol.,v. 68, no. 3, pp. 243-284.

Baedecker, M.J., Back, W.
1979(a): "Hydrogeological Processes and Chemical Reactions at a Landfill", Ground Water, v. 17, no. 5, pp. 429-437.

Baedecker, M. J., Back, W.
1979 (b): "Modern marine sediments as a natural analogue to the chemically stressed environment of a landfill", Journal of Hydrology, v. 43, pp. 393 - 414.

Belanger, D. W.
1984: " Groundwater velocity measurements using an electrical conductance borehole dilution device" MSc. project, unpublished, University of Waterloo, Waterloo, Ontario, 23 pp.

Cherry, J.A., Shaikh, A.V., Tallman, D.E., Nicholson, R.V.
1979: "Arsenic Species as an Indicator of Redox Conditions in Groundwater", J. Hydrol., v. 43, pp. 372-392.

Devlin J.F., Gorman, W.A.
in press: "The Distribution of Volatile Organics in a Leachate Plume, Gloucester, Ontario" Water Resources Research.

Farquhar, G.J., Rovers, F.A.
1973: Water Air and Soil Pollution, v. 2, pp. 483.

Farrington Lockwood Co. Ltd.
1983: "Final Report on Sampler Development, Standards Development and Volatile Organic Analysis for the Gloucester Special Waste Site Purge Well Demonstration Project", unpublished report submitted to Geological Testing Consultants, Ottawa, Canada, 34 pp.

Garrels, R.M., Christ, C.L.
1965: "Solutions Minerals and Equilibria", Harper and Row, New York, 450 pp.

Gartner Lee Associates Ltd.
1978: " Hydrogeologic study of the Gloucester Special Waste Disposal Site", Project No. 77-98 for the Department of Fisheries and Environment, 28 pp.

Hoeks, J., Borst, R.J.
"Anaerobic Digestion of Free Volatile Fatty Acids in soils Below Waste Tips", Water, Air and Soil Pollution, v. 17, pp. 165-173.

Jackson, R.E., Patterson, R.J.
1982: "Interpretation of pH and Eh Trends in a Fluvial Sand Aquifer System", Water Resources Research, v. 18, no. 4, pp. 1255-1268.

Jackson, R.E., Patterson, R.J., Graham, B.W., Bahr, J., Belanger, D., Lockwood, J., Priddle, M.
1985: "Contaminant Hydrogeology of Toxic Organic Chemicals at a Disposal Site, Gloucester, Ontario, 1. Chemical Concepts and Site Assessment", N.H.R.I. paper no. 23, Environment Canada, Ottawa, Ontario, 113 pp.

Light, T. S.
1972: "Standard solution for redox potential measurements", Analytical Chemistry, v. 44, No. 6, pp. 1038 - 1039.

Mackay, D.M., and Vogel, T.M.
1985: "Groundwater Contamination by Organic Chemicals: Uncertainties in Assessing Impact", presented at the Second Annual Canadian/American Conference on Hydrology: Hazardous Wastes in Groundwater - A Soluble Dilema; Banff, Alberta, Canada, June 25-28.

Nicholson, R.V., Cherry, J.A., Reardon, E.J.
1982: "Migration of Contaminants in Groundwater at a Landfill: A Case Study", J. Hydrol., v. 63, pp. 131-176.

Parsons F., Lage, G.B.
1985: "Chlorinated Organics in Simulated Groundwater Environments", J. Amer. Water Works Assoc., v. 77, no.5, pp. 52-59.

Roberts, P.V., McCarty, P.L., Roman, W.M.
1980: J. Water Pollut. Contr. Fed., v. 52, pp.161.

Rust, B.R., Romanelli, R.
1975: "Late Quaternary Subaqueous Outwash Deposits near Ottawa, Canada", in Glaciofluvial and Glaciolacustrine Sedimentation, A.V. Jopling and B.C. McDonald eds., Special Publication no. 23, pp. 177-192.

Stumm, W., Morgan, J.J.
1981: "Aquatic Chemistry", John Wiley and Sons, Toronto, 780 pp.

Wilson, B.H., Smith, G.B., Rees, J.F.
1986: "Biotransformations of Selected Alkylbenzenes and Halogenated Aliphatic Hydrocarbons in Methanogenic Aquifer Material: A Microcosm Study", Environ. Sci. Technol., v. 20, no. 10, pp. 997-1002.

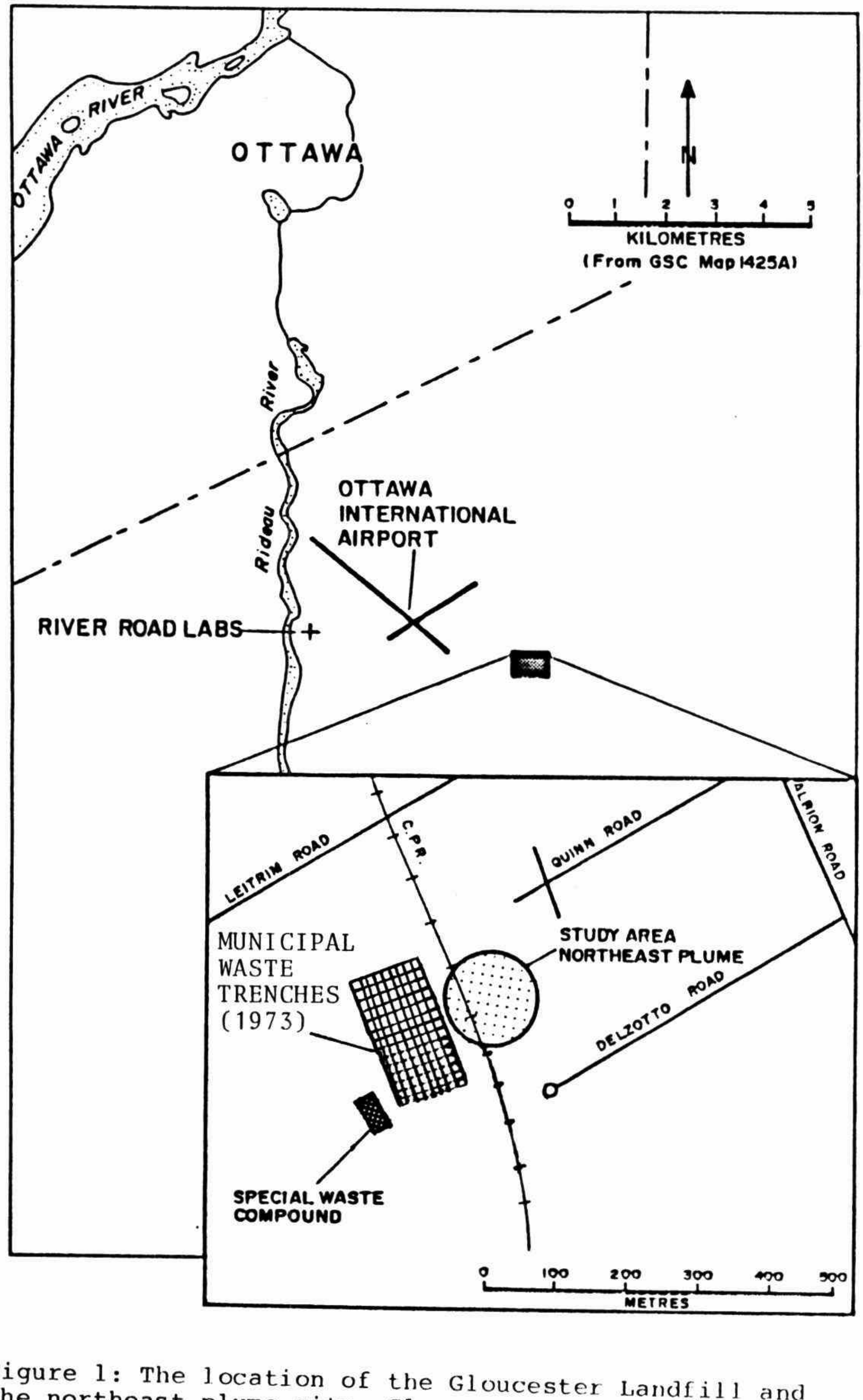


Figure 1: The location of the Gloucester Landfill and the northeast plume site, Gloucester, Ontario.

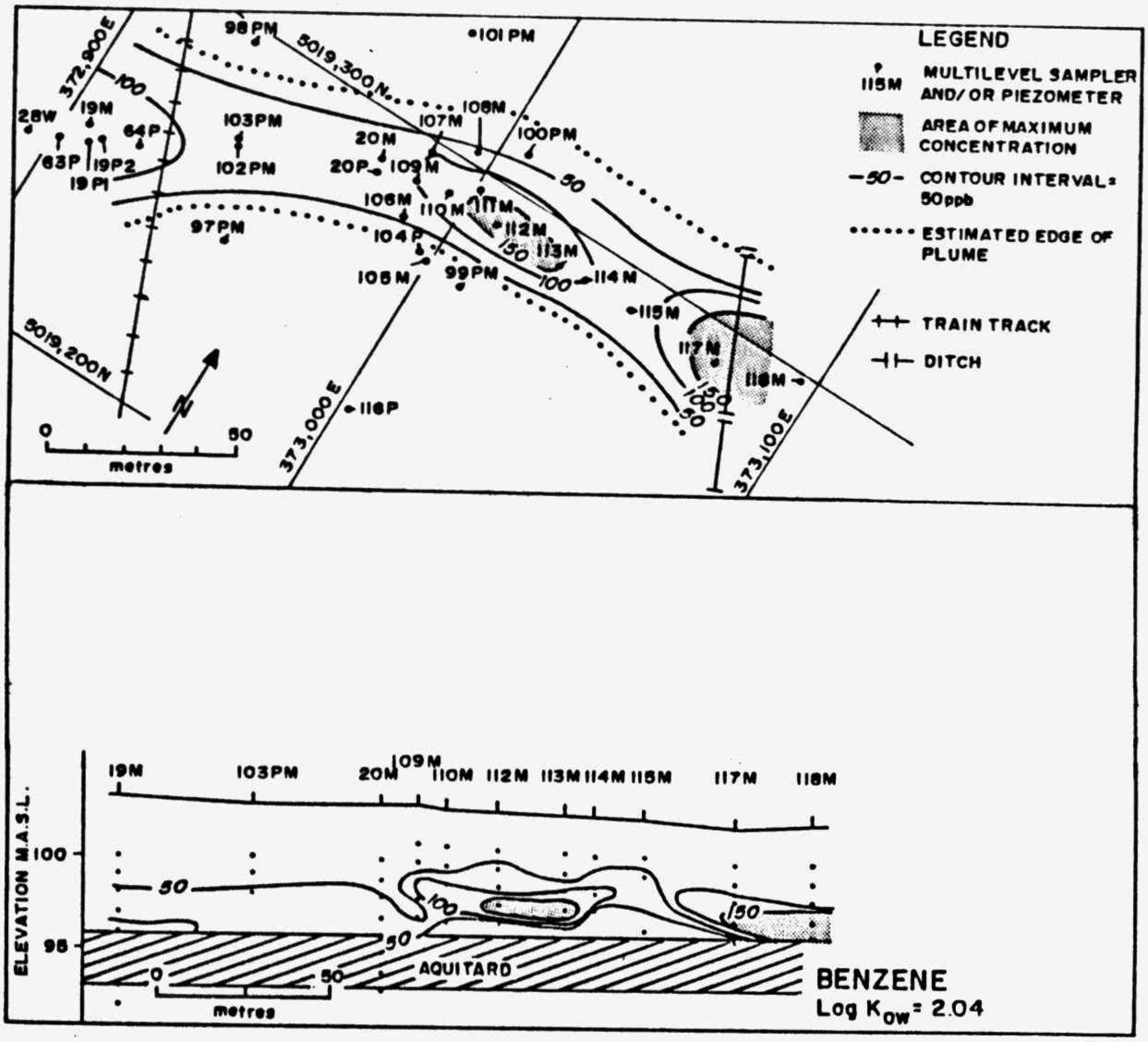


Figure 2: The distribution, in plan and section, of benzene at the northeast plume site.

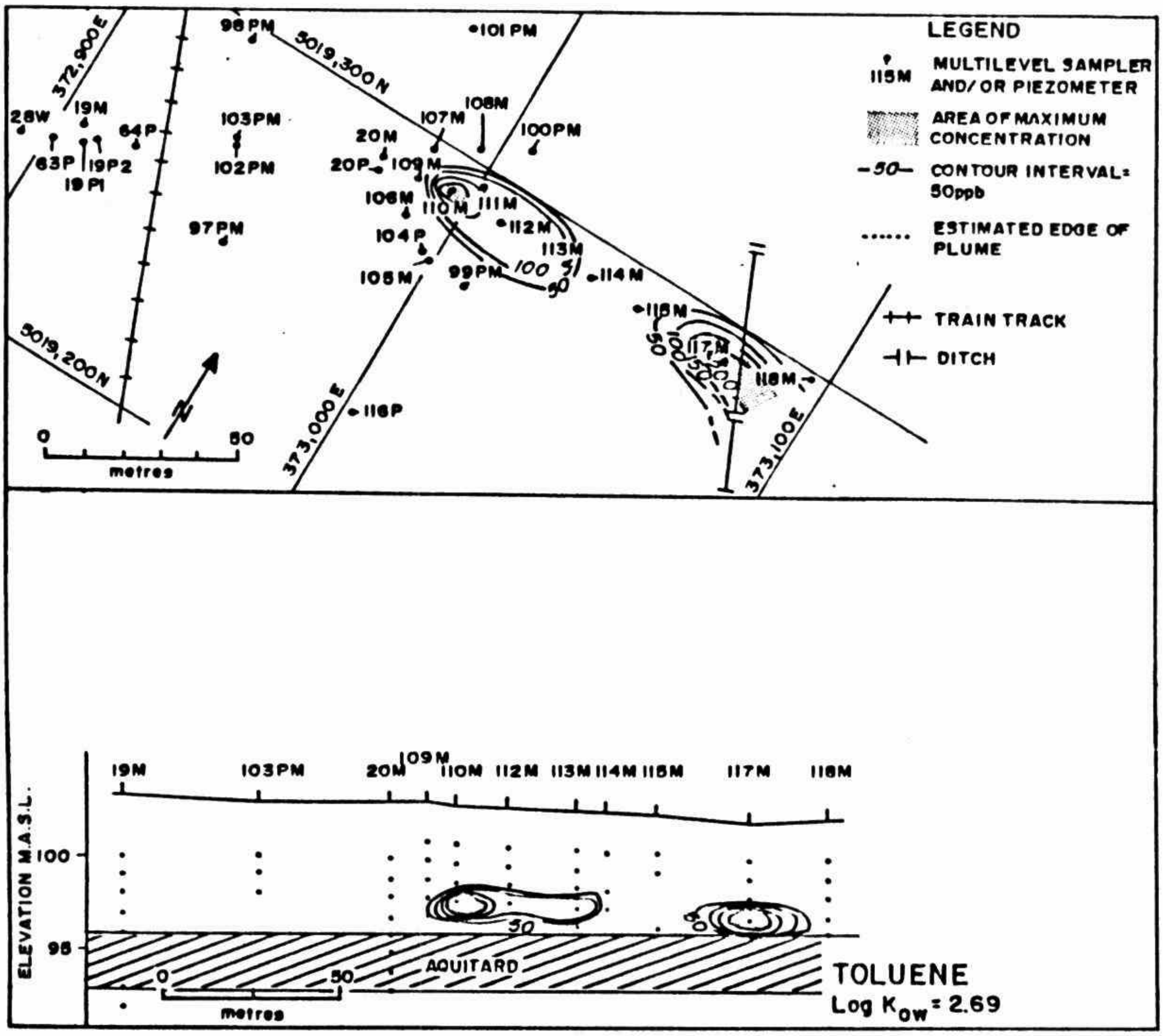


Figure 3: The distribution, in plan and section, of toluene at the northeast plume site.

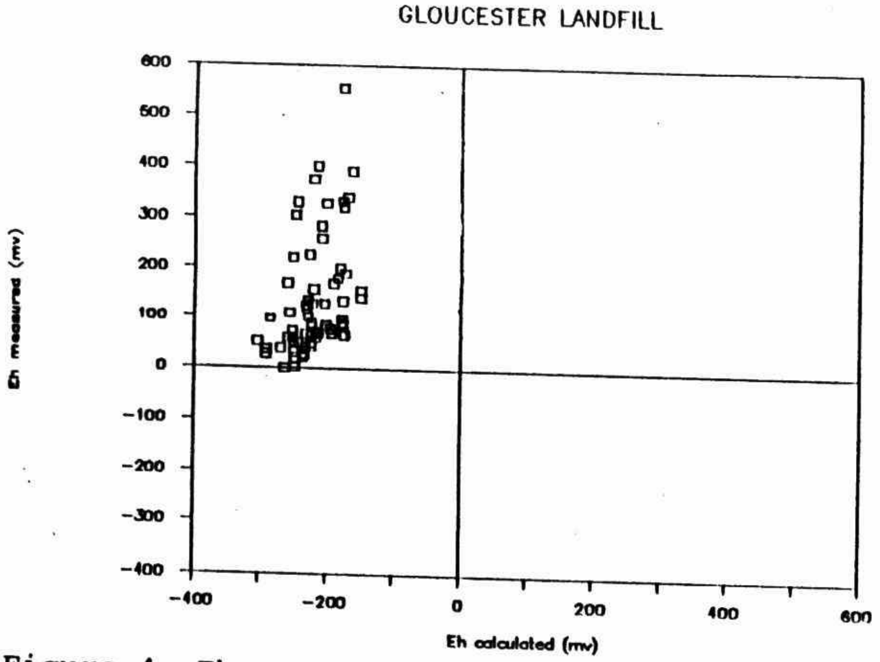


Figure 4: Eh measured (Pt electrode) vs. Eh calculated ($H_2S/SO_4^=$).

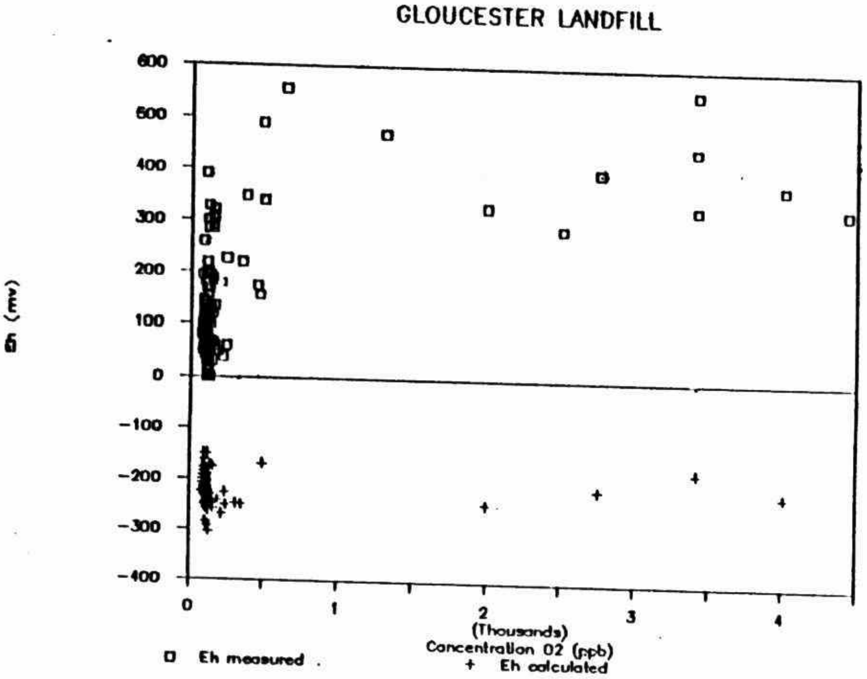


Figure 5: Eh measured (Pt electrode) vs. dissolved oxygen concentration.

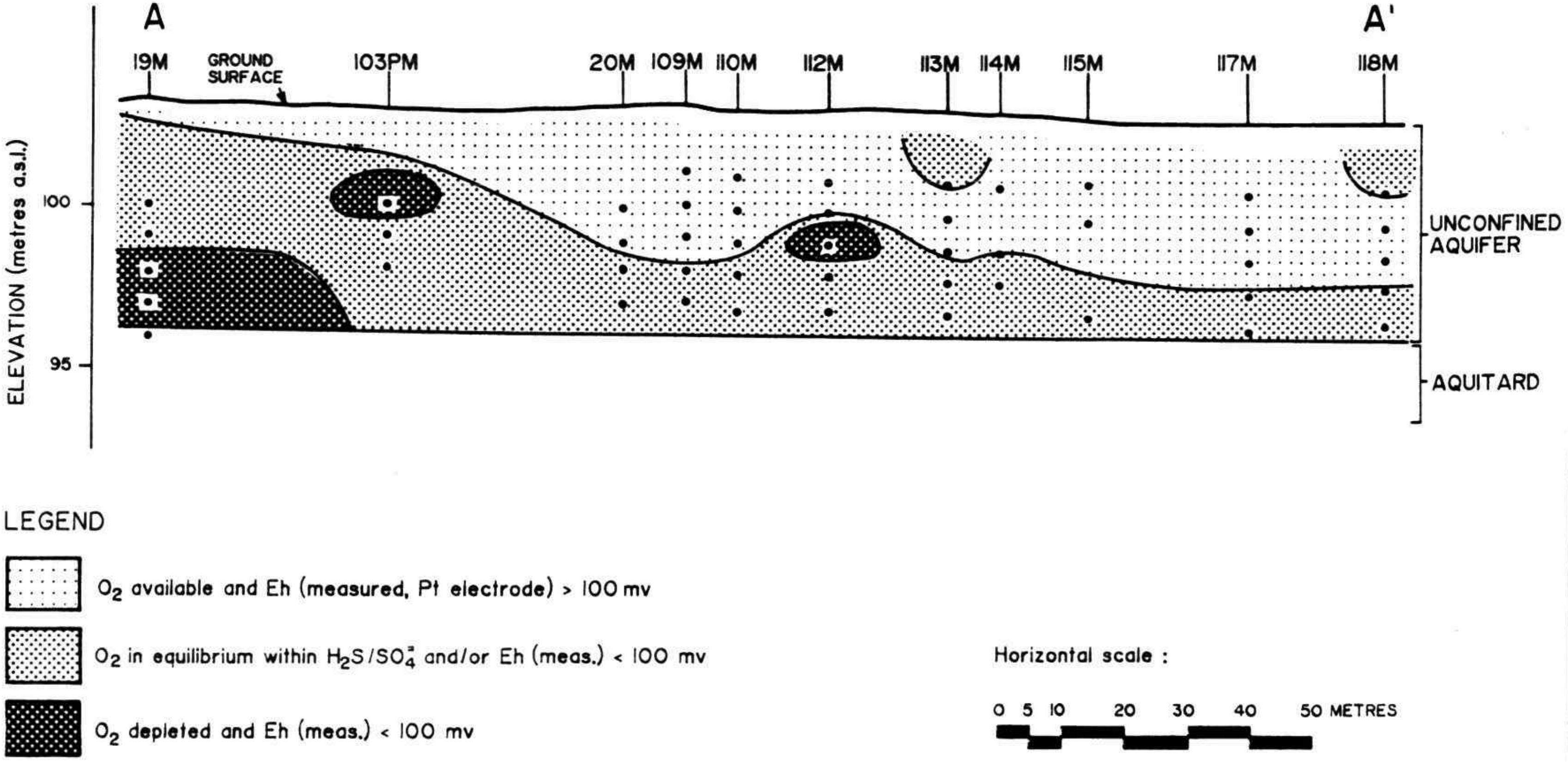

A
A'
19M
GROUND SURFACE
103PM
20M
109M
110M
112M
113M
114M
115M
117M
118M
ELEVATION (metres a.s.l.)
100
95
UNCONFINED AQUIFER
AQUITARD
LEGEND
O_2 available and Eh (measured, Pt electrode) > 100 mv
O_2 in equilibrium within $H_2S/SO_4^=$ and/or Eh (meas.) < 100 mv
O_2 depleted and Eh (meas.) < 100 mv
Horizontal scale :
0 5 10 20 30 40 50 METRES

FIGURE 6

REDOX ZONES WITHIN THE NORTHEAST PLUME

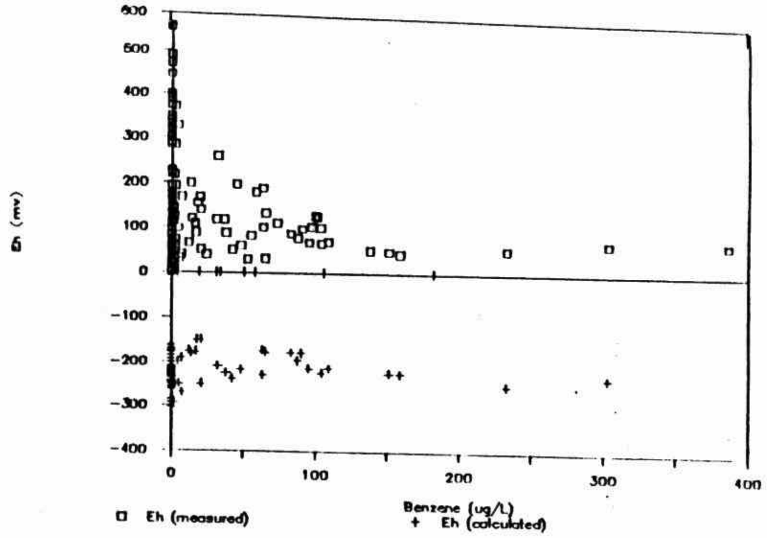


Figure 7: Eh vs. concentration benzene.

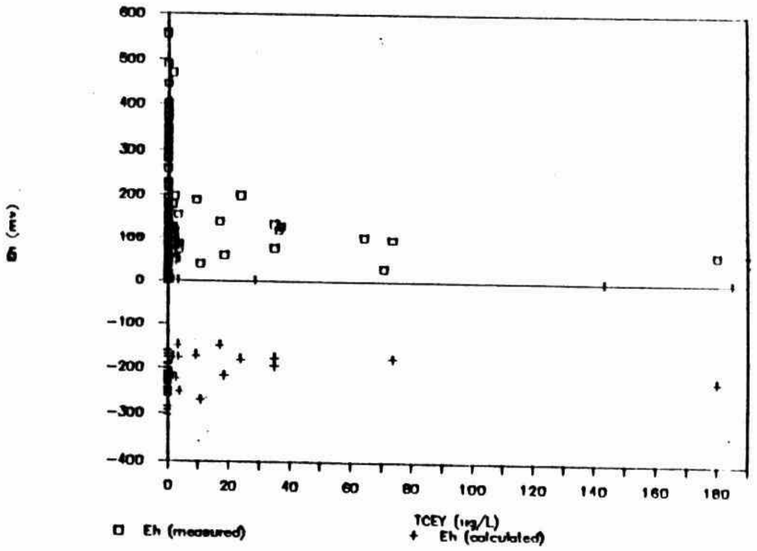


Figure 8: Eh vs. concentration trichloroethene

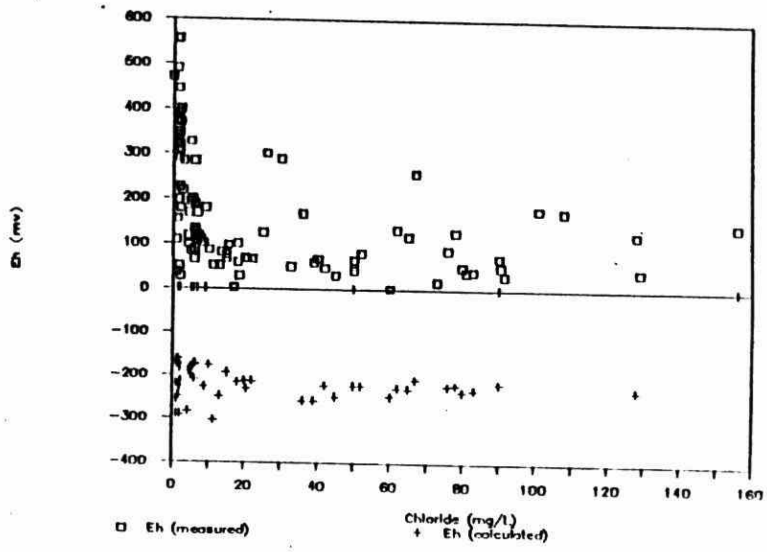
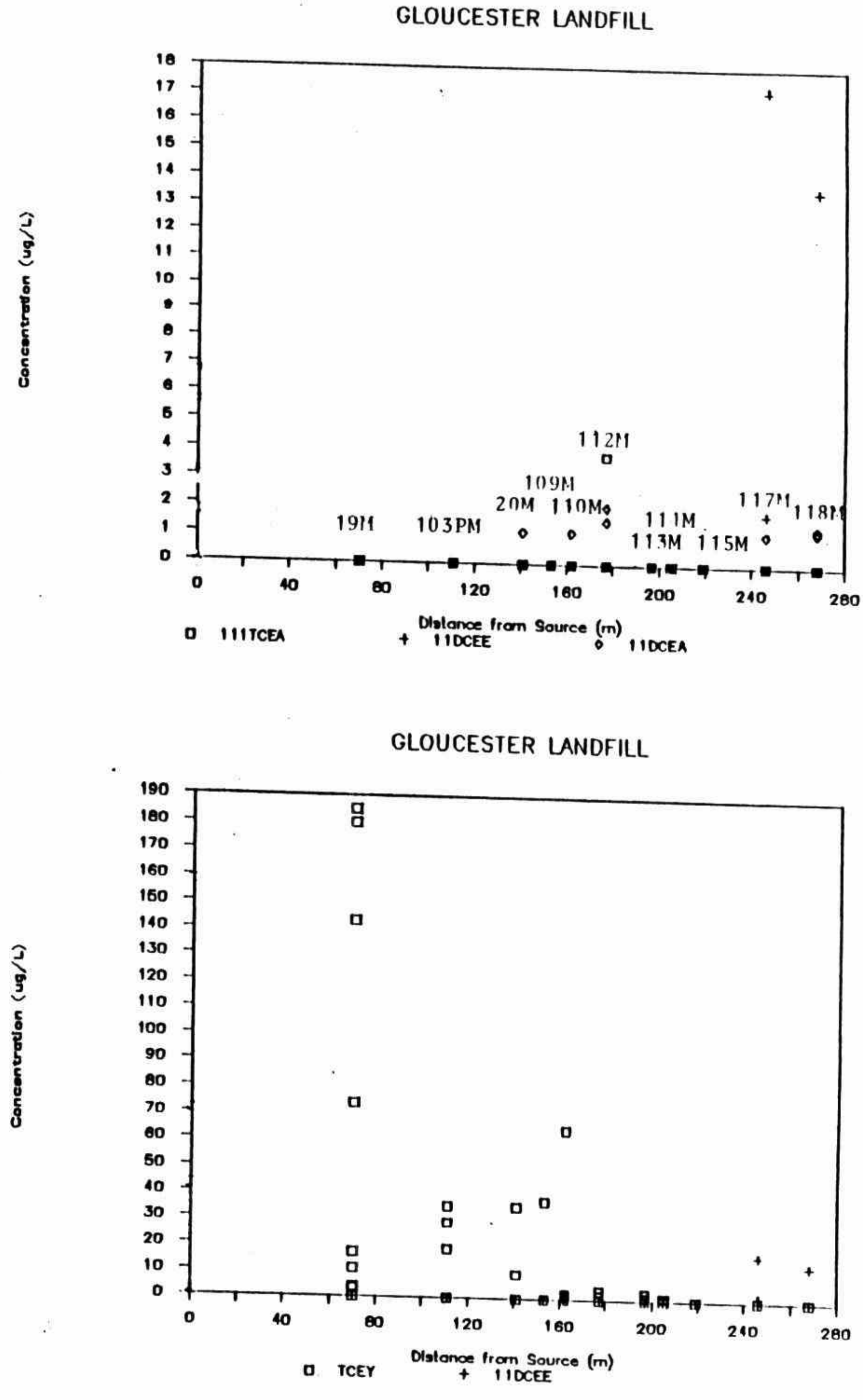


Figure 9: Eh vs. concentration chloride.



Figures 10 and 11: The concentrations of possible parent-daughter compounds through the middle of the plume.

EFFECTS OF INCREASING AMOUNTS OF NON-POLAR ORGANIC LIQUIDS IN DOMESTIC WASTE LEACHATE ON THE HYDRAULIC CONDUCTIVITY OF CLAY LINERS IN SOUTHERN ONTARIO

by

R.M. Quigley, F. Fernandez and E. Yanful
Geotechnical Research Centre
Faculty of Engineering Science
The University of Western Ontario
London, Canada, N6A 5B9

MOE Project No. 213PL

Technology Transfer Conference No. 7
Paper No. 67, Session C
December 8-9, 1986
Toronto, Ontario

EFFECTS OF INCREASING AMOUNTS OF NON-POLAR ORGANIC LIQUIDS IN DOMESTIC WASTE LEACHATE ON THE HYDRAULIC CONDUCTIVITY OF CLAY LINERS IN SOUTHERN ONTARIO

R.M. Quigley, F. Fernandez and E. Yanful
Geotechnical Research Centre
Faculty of Engineering Science
The University of Western Ontario
London, Canada, N6A 5B9

ABSTRACT

Organic liquids, less polar than water, are capable of producing dramatic changes in the structure of clayey soils and their hydraulic conductivity. Double layer theory is adequate to explain the behaviour of pure liquid-clay mixtures, however, it fails to fully account for the behaviour of water-compacted clays sequentially permeated by water and organic liquids. The "hydrophobic" nature of non-polar liquids such as cyclohexane and benzene, restricts their flow to larger channels through the pore system, resulting in decreases in **k** and with little effect on the double layers of water. The values of **k** seem to be dependent on the hydraulic gradient applied (non-Darcian behaviour) and threshold gradients may be measured below which breakthrough and flow do not occur. Viscosity plays an important role on the behaviour of water-soluble permeants such as ethanol, producing an initial decrease followed by gradual increases in **k** to equilibrium values that are practically independent of the hydraulic gradient used.

The addition of organic liquids induced rapid flocculation of the otherwise stable suspended matter in domestic waste leachate, the rate of flocculation being more pronounced with increasing abundance of organic liquids. Inorganic salts also precipitated resulting in a decrease in salinity of the clear leachate phase. The physical location of the flocs (as floaters or sinkers) depends on the amount and type of organic liquid added. Solubility limits mean that large amounts of most non-polar organics will generally produce two liquid phases.

Preliminary testing on water-compacted brown Sarnia soil using the clear phase of domestic leachate containing up to 45% ethanol and 5% benzene has yielded no significant increases in k. Furthermore, leachate spiked with 20% ethanol produced a decrease in **k** that is believed to be due to its higher viscosity. Mercury intrusion porosimetry results are presented to illustrate the very different soil fabric produced by moulding with organic/water mixtures compared to pure water.

INTRODUCTION

This paper reports on the results and problems encountered during the first year of study on the effects of organic liquids in domestic waste leachate on the hydraulic conductivity of southern Ontario brown soils. This presentation should be read in association with a preliminary paper presented by Quigley and Fernandez (1985) in the Proceedings of the 6th Technology Transfer Conference sponsored by the Ontario Ministry of the Environment. The nature of the Sarnia test soils and the importance of organics was outlined in the preliminary paper.

ORGANIC/LEACHATE INTERACTION

Flocculation and Phase Separation

Initial experiments involved addition of relatively large amounts of organic liquids to domestic waste leachate from London's Westminster landfill site. A schematic drawing of these mixtures after sitting for 18 hours is shown on Figure 1. The hatched regions represent the dark brown flocs, the dotted zones represent stable suspended matter and the open zones represent clear liquid. Except for influent 1 in Bottle #1, which was untreated leachate, the clear liquid phase in each mixture was separated and used as a permeant in hydraulic conductivity tests, as described by Quigley and Fernandez (1985). In mixtures 2 and 3 only one liquid phase is present due to the complete solubility of ethanol in the leachate. The stable suspended matter in the raw leachate (Bottle #1) is flocculated upon addition of ethanol, the flocs then settling to the bottom as shown by Bottles 2 and 3. In mixture 4, the flocs are "dragged" upwards by benzene resulting in an upper "benzene rich" phase and a lower aqueous phase. It appears from the scale dimensions in Figure 1 that the amount of suspended sediment that flocculates increases with increase in the amount of organic liquid. Also, the physical location of the flocs (as floaters or sinkers) appears from Figure 1 to be a function of the amount and type of organic liquid added.

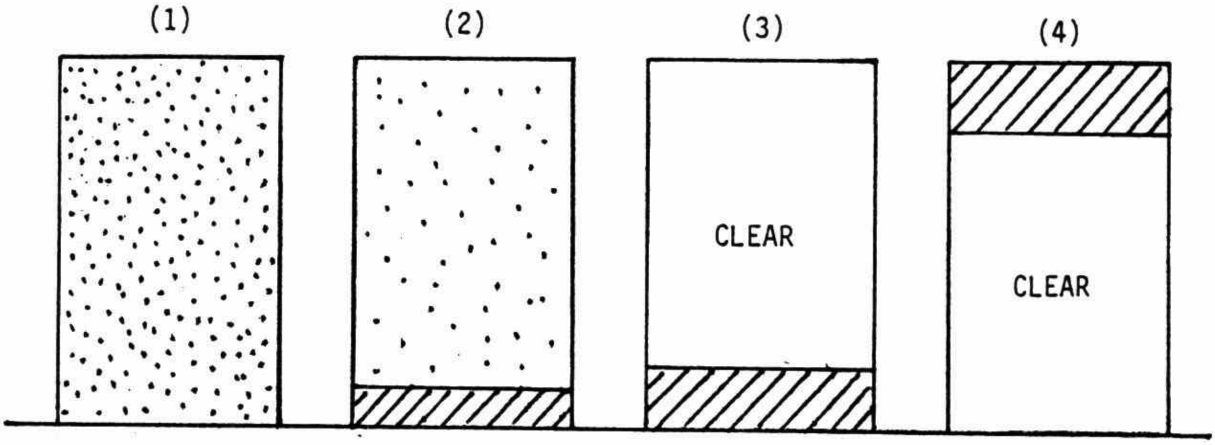


FIGURE 1. LEACHATE/ORGANIC MIXTURES AT 18 HOURS

(1)	100% LEACHATE.	DARK BROWN STABLE DISPERSED SUSPENSION
(2)	80:20 LEACHATE:ETHANOL.	DARK BROWN FLOCS AT BOTTOM OF MEDIUM BROWN SEMI-CLEAR SUSPENSION
(3)	60:40 LEACHATE:ETHANOL.	DARK BROWN FLOCS AT BOTTOM OF CLEAR SOLUTION
(4)	40:50:10 LEACHATE:ETHANOL:BENZENE.	MEDIUM BROWN FLOCS FLOATING ON CLEAR SOLUTION

Although the flocculation resulting from addition of organics surprised us, it is totally logical chemically, and considerable work is now under way to establish what components of the original leachate separate out with the flocculated phase. The results of our preliminary work are presented in four tables in Appendix A.

Viscosity Alteration

During start-up of this project, we discovered that dramatic changes in solution viscosity occur when alcohols and water are mixed. Figure 2 illustrates this well known chemical phenomenon for mixtures of both methanol and ethanol in water at 20°C. The ratio of mixture viscosity to water viscosity increases with increasing alcohol content to a maximum at an alcohol content of about 40%. As the alcohol content is increased beyond 40%, the viscosity decreases to values for pure alcohol. It is clear from Figure 2 that, up to about 25% alcohol content, the increase in the viscosity is more pronounced for ethanol than for methanol. The influence of these viscosity changes on the hydraulic conductivity is discussed in the next section.

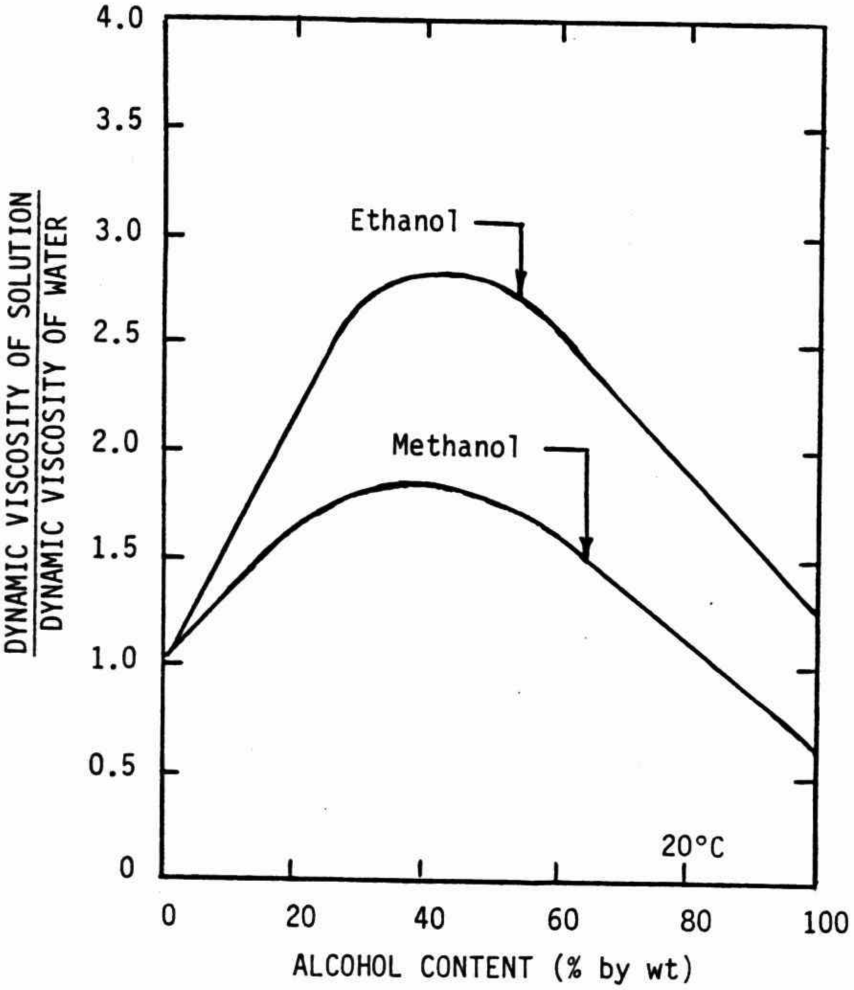


FIGURE 2. RELATIVE VISCOSITY OF AQUEOUS SOLUTIONS CONTAINING ALCOHOLS (Handbook of Chemistry and Physics, CRC, 56th Edition)

HYDRAULIC CONDUCTIVITY

Previous Work

Figure 3, taken directly from Bowders et al (1986), shows that the variation in hydraulic conductivity of compacted kaolinite permeated with solutions of varying amounts of methanol in water may be related to the viscosity curve for methanol shown on Figure 2. It is clear that for both fixed-wall and flexible-wall cells, the hydraulic conductivity decreases as the permeant becomes more viscous

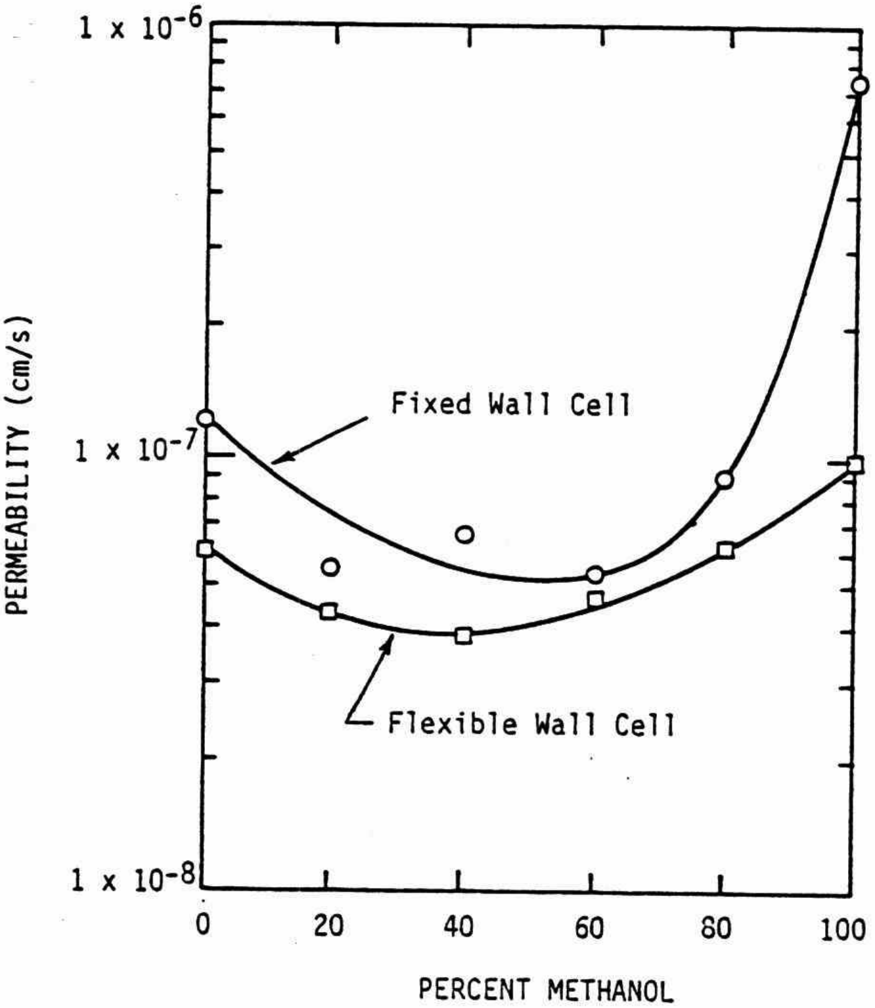


FIGURE 3. PERMEABILITY OF COMPACTED KAOLINITE TO AQUEOUS SOLUTIONS CONTAINING METHANOL (Directly from Bowders et al, 1986)

due to the addition of methanol. When the methanol content of the permeant exceeds 50% or so, the viscosity of the permeant decreases again and flow through the pores increases. The hydraulic conductivity obtained from the fixed-wall cell is higher than that obtained from the flexible-wall cell, irrespective of the methanol content of the permeant. This may be explained by flow along the sides of the fixed-wall cell. In our experiments, an effective stress is applied to the soil and lateral yield has successfully prevented side-wall leakage.

The hydraulic conductivity, **k** (cm/s) of the same kaolinitic soil permeated with methanol/water mixtures is replotted on Figure 4a. When the effects of viscosity are removed by plotting the intrinsic permeability, K (cm^2) the soil shows little change in K as the amount

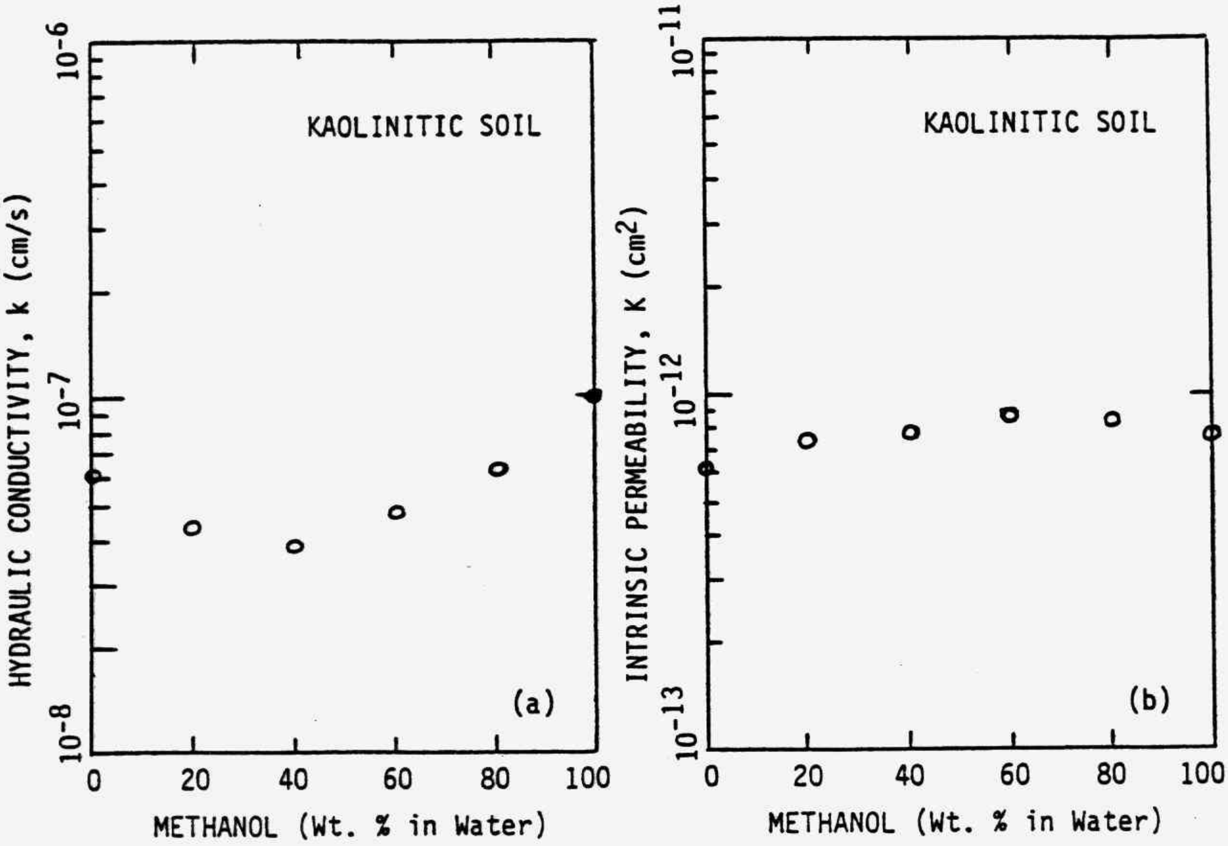


FIGURE 4. HYDRAULIC CONDUCTIVITY AND INTRINSIC PERMEABILITY VS PERCENT METHANOL IN WATER (a) DIRECTLY FROM DANIELS & LILJESTRAND, 1984; (b) REPLOTTED FROM DANIELS & LILJESTRAND, 1984

of methanol in water is increased from 20 to 80 percent (Figure 4b). Clearly for this inactive soil, viscosity changes control the changes in hydraulic conductivity, and not changes in the behaviour of the clay itself.

Current Hydraulic Conductivity Studies

Water/Alcohol/Clay Systems

Similar plots obtained for the Sarnia brown clayey silt compacted at a constant void ratio of 0.80 are shown in Figures 5a and 5b. A major difference in compaction procedures was employed, however, the soil being compacted and permeated with the alcohol/water mix shown. Figure 5a shows that up to about 40% ethanol, the hydraulic

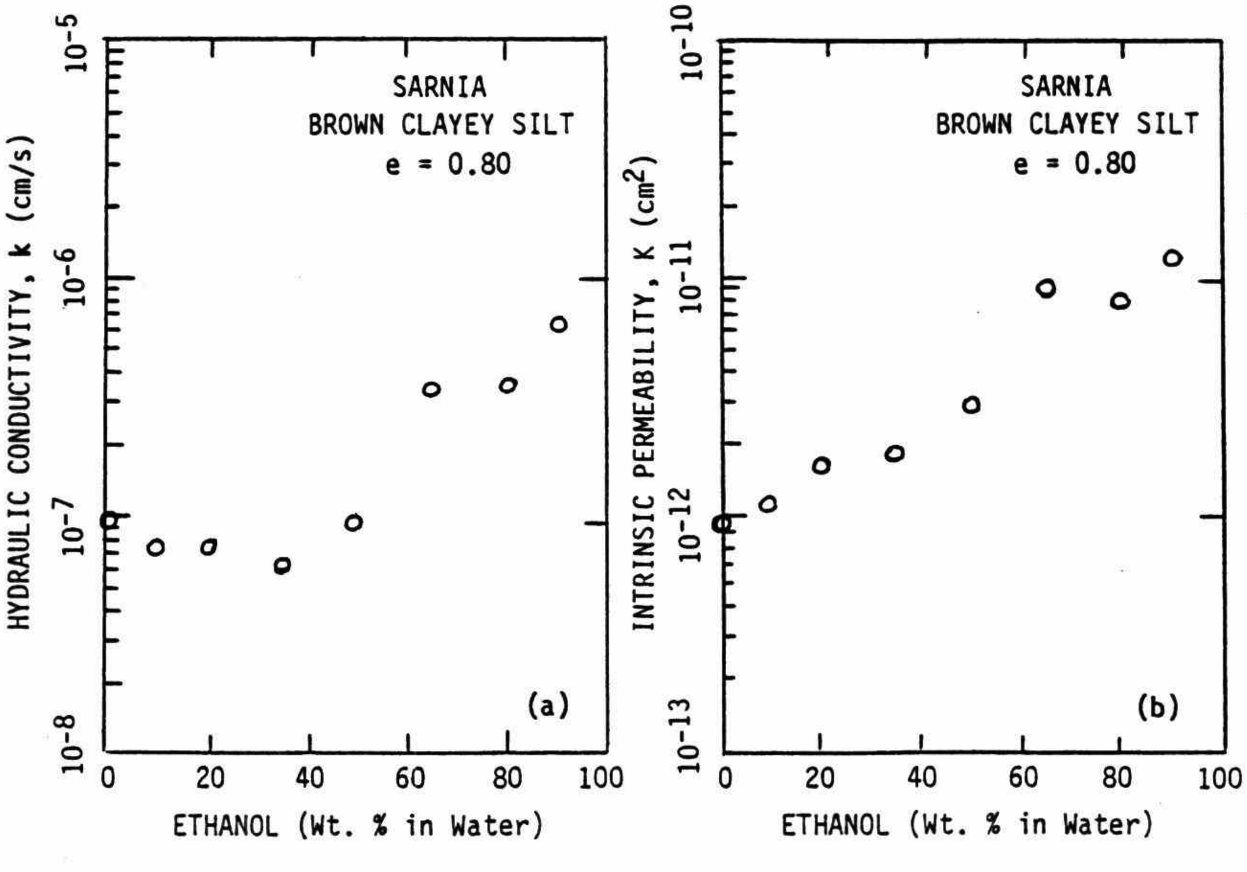


FIGURE 5. HYDRAULIC CONDUCTIVITY AND INTRINSIC PERMEABILITY VS PERCENT ETHANOL IN WATER (COMPACTED AND PERMEATED WITH MIX SHOWN)

conductivity decreases slightly and then increases by nearly an order of magnitude as the amount of ethanol was increased to 90%. The companion plot of intrinsic permeability vs percent ethanol in water (Figure 5b), however, shows an increase in K with increasing amounts of ethanol in water. Thus the Sarnia brown clayey silt, rich in illite, chlorite and smectite behaves differently from the kaolinitic soil used by Daniels and Liljestrand (1984). Since the kaolinitic soil is believed to have been compacted with water and then permeated with the water/alcohol mixtures the results are not strictly comparable to the Sarnia soil results. This matter is discussed further in the porosimetry section.

The rapid increase in intrinsic permeability (Figure 5b) is believed to be due to double layer contraction by the presence of alcohol (lower dielectric constant than water) plus soil flocculation and ped/macropore formation prior to and during compaction.

Leachate/Alcohol/Clay Systems

Four hydraulic conductivity tests carried out on water compacted soils, using the selected permeants described in the previous sections are shown on Figures 6 to 9. The soil was brown silty clay from 0.3 m depth whose clay minerals consist mainly of illite, chlorite and up to 10% smectite (see detailed composition in Quigley and Fernandez, 1985).

Figure 6a (adapted from Quigley and Fernandez, 1985) indicates that natural domestic landfill leachate causes a slight decrease in **k** from ~ 2.0×10^{-9} cm/s to ~ 1.8×10^{-9} cm/s (leachate) in spite of extensive K^+ fixation and retardation shown by Figure 6b. The retardation of Na^+ and K^+ results in desorption of Ca^{++} and Mg^{++} resulting in effluent concentrations far above influent values.

On Figure 7a, the results of testing using leachate spiked with 20% ethanol as the permeant are presented. They indicate that **k** decreases from ~ 5.4×10^{-9} cm/s (water) to 3.3×10^{-9} cm/s (spiked leachate). This small decline in **k** appears compatible with observed viscosity increases at this concentration of alcohol in water. The effluent ethanol concentration curve (Figure 7b) shows early arrival and some tailing indicating channel flow, although effective replacement of the original pore water by the ethanol-spiked permeant

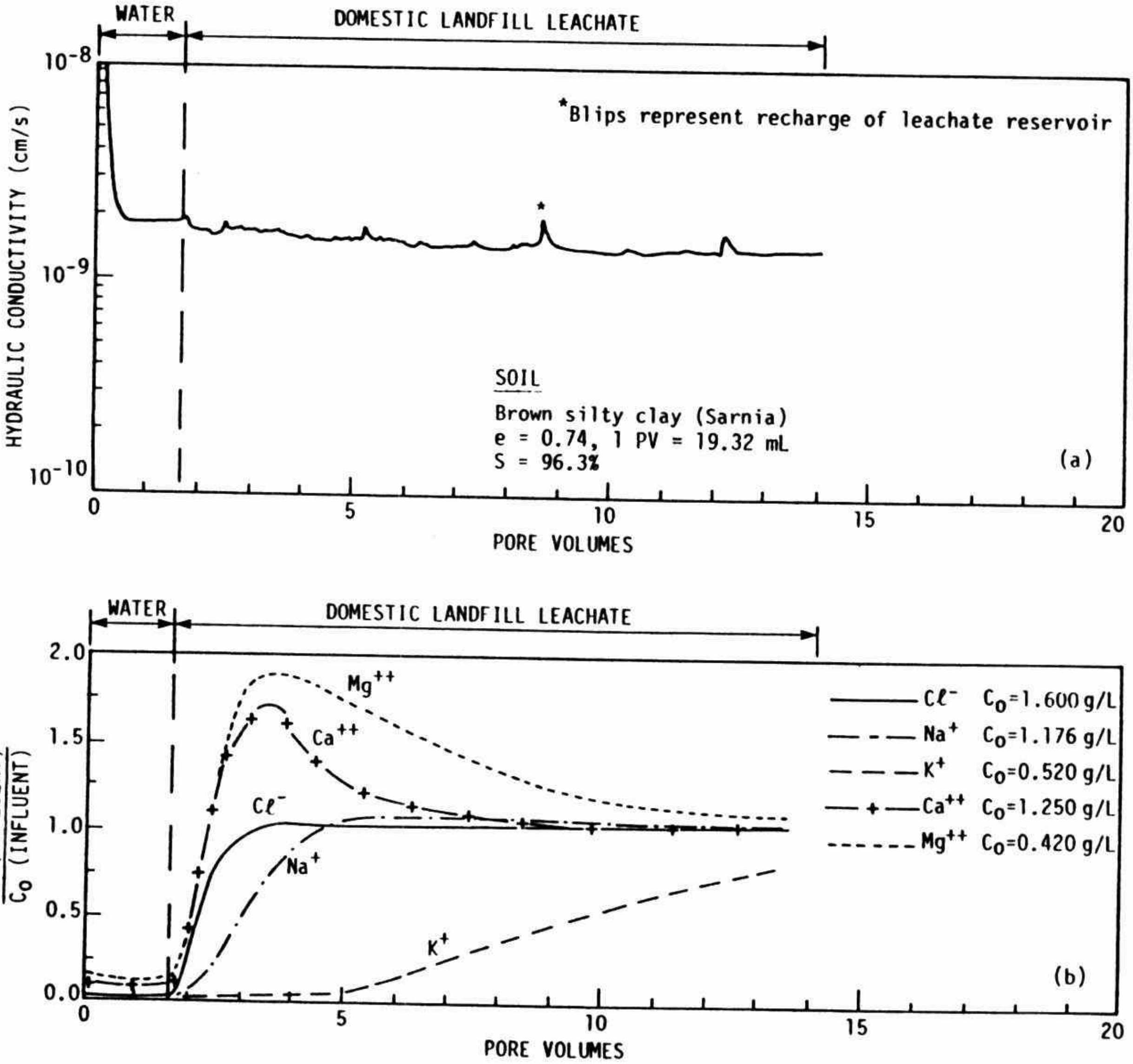


FIGURE 6. SOIL/DOMESTIC LEACHATE COMPATIBILITY: (a) HYDRAULIC CONDUCTIVITY, (b) EFFLUENT CHEMISTRY VS PORE VOLUMES OF LEACHATE; WEATHERED SARNIA SOIL, 0.3 m DEPTH, COMPACTED, VOID RATIO = 0.74

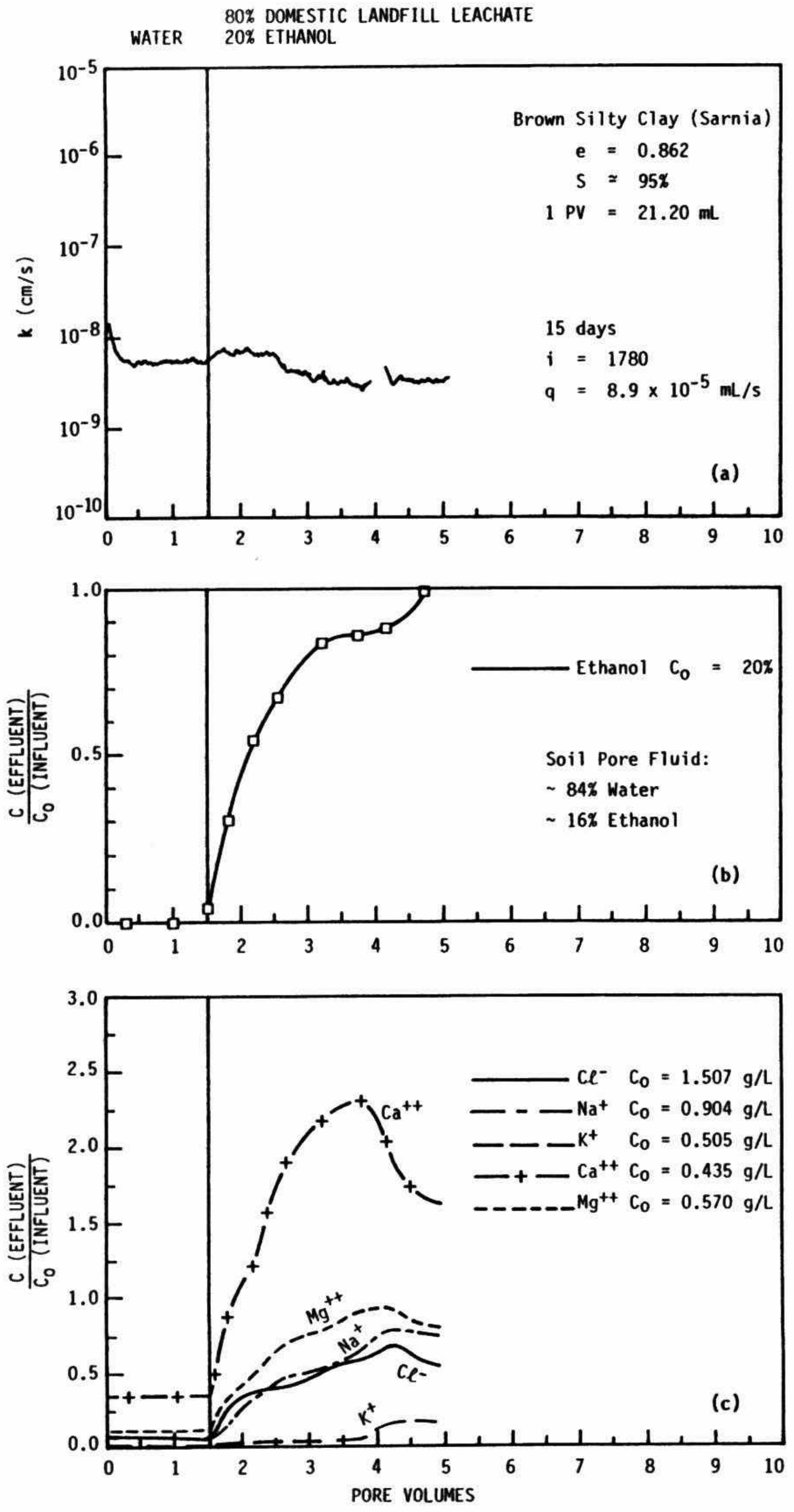


FIGURE 7. SOIL-LEACHATE COMPATIBILITY (PERMEANT 2); (a) HYDRAULIC CONDUCTIVITY AND EFFLUENT CHEMISTRY FOR (b) ORGANIC AND (c) IONIC SPECIES VS PORE VOLUMES OF PERMEANT PASSED THROUGH

appears to have occurred. Post-testing analysis of the pore fluid (extracted by distillation from the soil revealed that it contained ~ 16% ethanol, which compares favourably with the 20% ethanol concentration of the influent leachate.

The test using leachate spiked with 40% ethanol as the influent permeant (Figure 8a) resulted in a slight increase in **k** from ~ 5.7×10^{-9} cm/s (water) to ~ 6.9×10^{-9} cm/s (spiked leachate). In contrast, the leachate spiked with 45% ethanol and 5% benzene produced a slight decrease in **k** from ~ 6.2×10^{-9} cm/s to ~ 4.0×10^{-9} cm/s after about 3 pore volumes of leachate flow (Figure 9a).

The effluent concentration curves for ethanol shown in Figure 8b and 9b are both similar to that for the leachate spiked with 20% ethanol (Figure 7b). The respective post-testing ethanol concentrations in the soil pore fluids are ~ 32% and ~ 36%. These values correspond to ~ 80% of the ethanol concentration in the respective influent indicating extensive replacement of the original pore water.

The effluent concentration curve for benzene (Figure 9b) displays an irregular pattern suggestive of evaporation losses in the effluent collection bottles. The C/C_0 for benzene reached 0.5 after 3.3 pore volumes of leachate flow and never did reach full influent values. The final benzene value in the pore fluid was only ~ 2% corresponding to less than 50% of the influent value.

The effluent concentration curves for Cl^- and soluble cations (Na^+, K^+, Ca^{++} and Mg^{++}) are presented in Figures 6c, 7c, 8c and 9c. The curves for the present series of tests (Figures 7c, 8c and 9c), in particular, illustrate the following features:

a) Potassium is strongly attenuated and C/C_0 does not exceed 20% of the corresponding influent values. This behaviour is akin to that shown by pure landfill leachate (Figure 6c).

b) The sodium and chloride curves show an irregular and strongly tailed behaviour indicating channel flow.

c) The early arrival and "hardness halo" effect shown by calcium and magnesium for pure leachate (Figure 6c) is

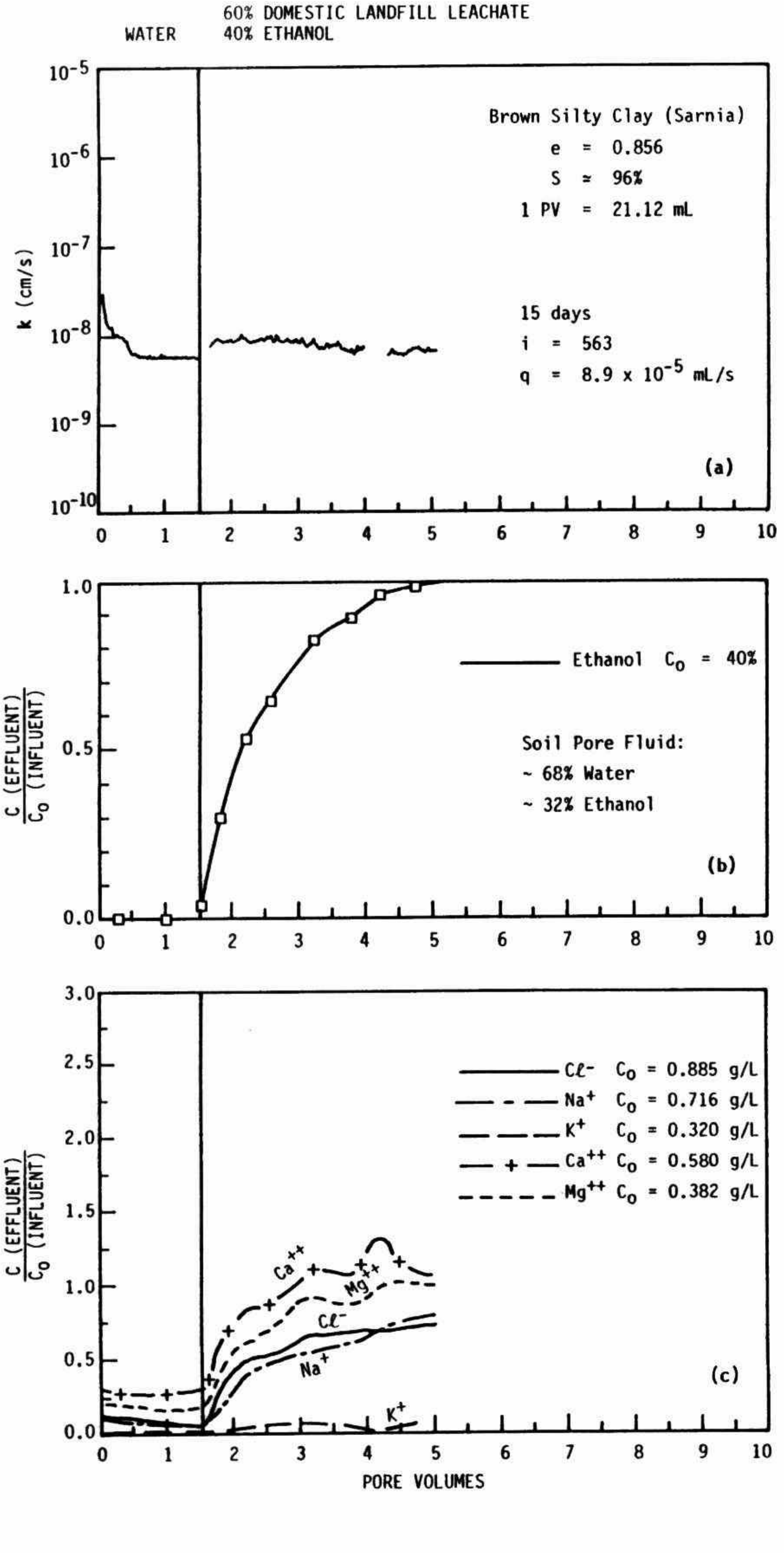


FIGURE 8. SOIL-LEACHATE COMPATIBILITY (PERMEANT 3); (a) HYDRAULIC CONDUCTIVITY AND EFFLUENT CHEMISTRY FOR (b) ORGANIC AND (c) IONIC SPECIES VS PORE VOLUMES OF PERMEANT PASSED THROUGH

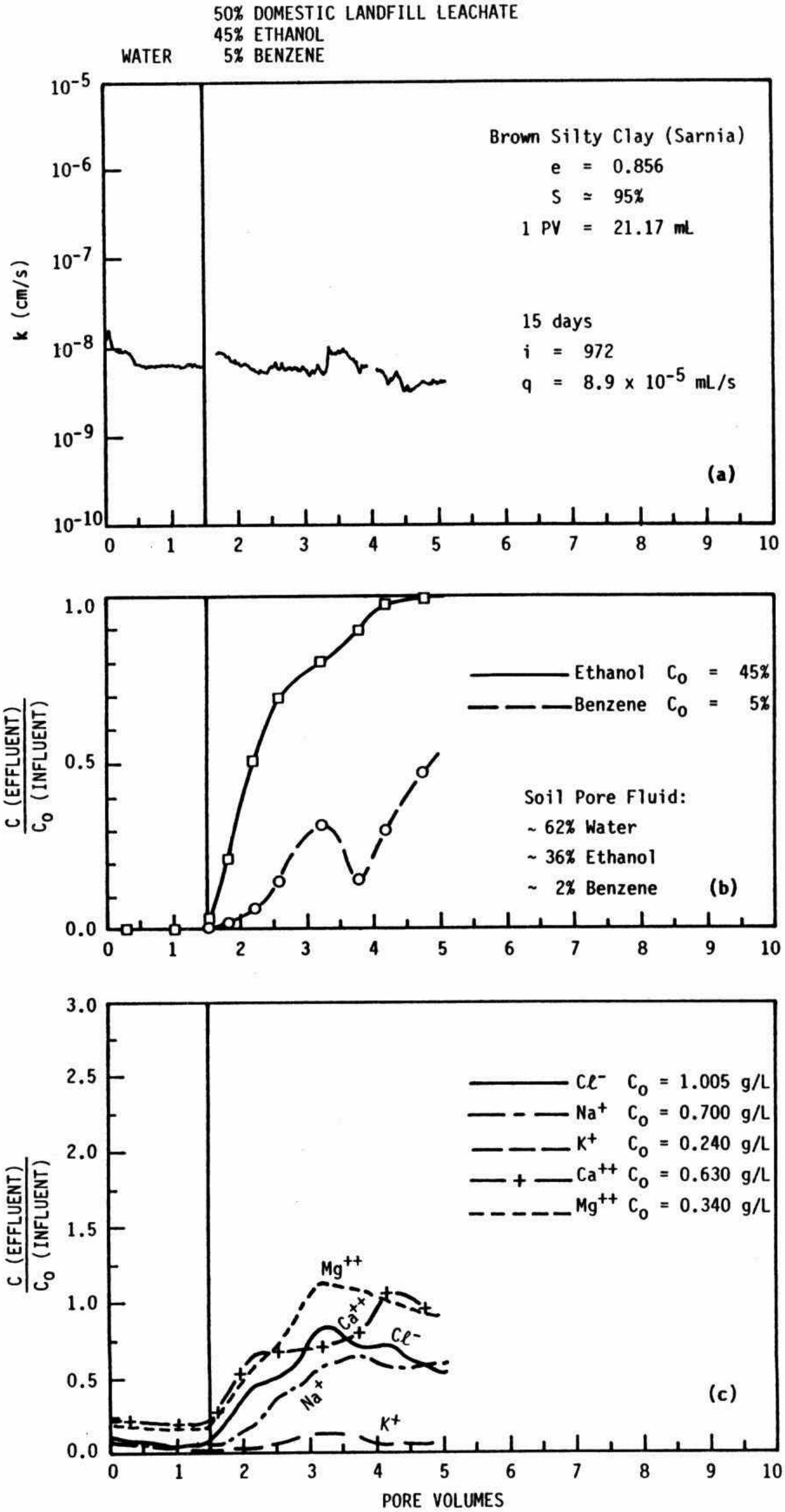


FIGURE 9. SOIL-LEACHATE COMPATIBILITY (PERMEANT 4); (a) HYDRAULIC CONDUCTIVITY AND EFFLUENT CHEMISTRY FOR (b) ORGANIC AND (c) IONIC SPECIES VS PORE VOLUMES OF PERMEANT PASSED THROUGH

exhibited only by calcium in the sample permeated with leachate spiked with the least amount (20%) of alcohol (Figure 7c). At higher alcohol contents, the desorption of Ca^{++} and Mg^{++} appears to be strongly muted. Inspection of influent permeant composition (Table I, Appendix A), however, indicates that the Na^{+} and especially K^{+} are greatly reduced from the original leachate values due to the addition of alcohol. The intensity of desorption may have been reduced in large part by the reduction in alkali content of the influent. Ion balance calculations had not been performed at the time of preparation of this paper.

POROSIMETRY CONTROLS

The engineering behaviour of clayey soils is controlled in large measure by the soil structure inherited from its depositional environment. Compacted soils are similar in that the moulding liquid mixed with the soil before compaction should have a greater effect on fabric and soil structure than many post-compaction permeants.

For example, the Sarnia soils compacted with pure water and then permeated with 20% ethanol/80% leachate yielded a single, very dominant pore size mode of 0.08 μm as shown on Figure 10. The mode itself was defined by high pressure mercury intrusion into freeze-dried samples. When the same soil was compacted with 10% ethanol/90% water, the major pore size mode increased to 0.24 μm with a very broad range of smaller pores (Figure 11). Finally, a moulding fluid of 65% ethanol/35% water yielded a very flocculated structure with some large pores such as that shown by the minor mode at 16.13 μm on Figure 12.

It is these large interped pores which probably produced part of the increased **k** values shown on Figure 5 for the higher alcohol contents in the influent aqueous solutions.

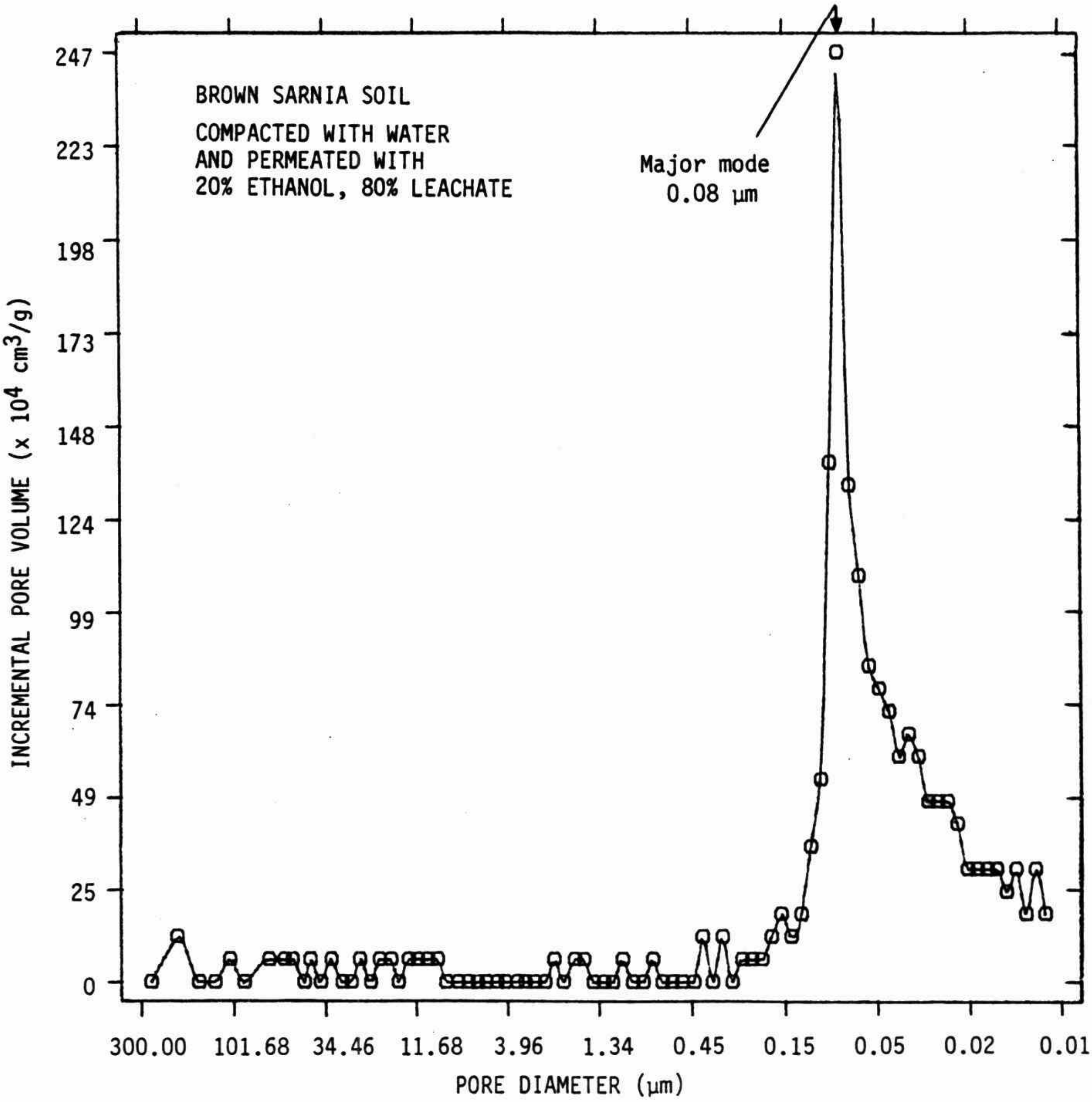


FIGURE 10. POST TESTING ASSESSMENT OF PORE SIZE DISTRIBUTION OF TEST SOILS MOULDED AND COMPACTED WITH WATER THEN PERMEATED WITH MIXTURE OF 20% ETHANOL AND 80% LEACHATE

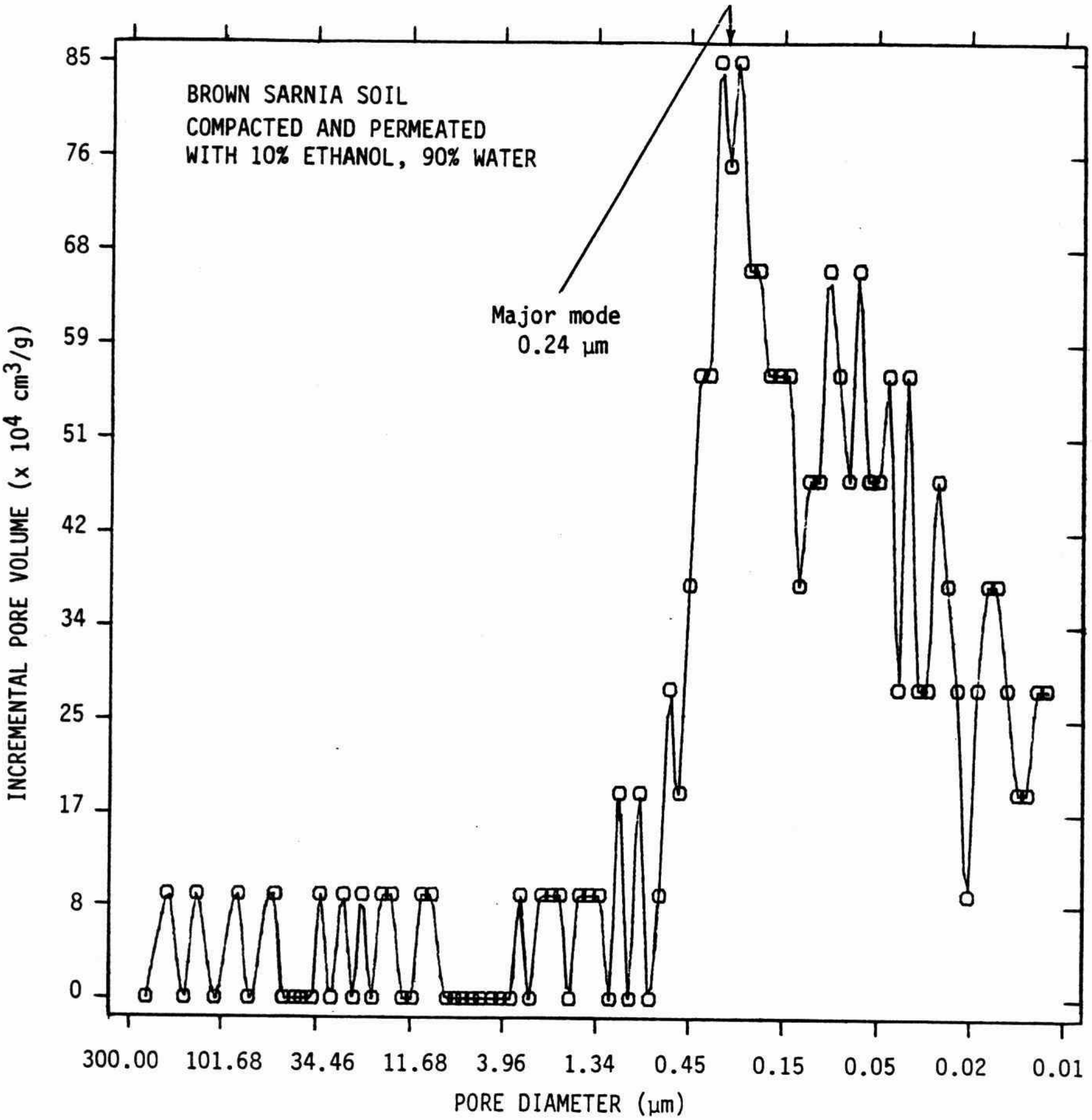


FIGURE 11. POST TESTING ASSESSMENT OF PORE SIZE DISTRIBUTION OF TEST SOILS MOULDED, COMPACTED AND PERMEATED WITH 10% ETHANOL AND 90% WATER

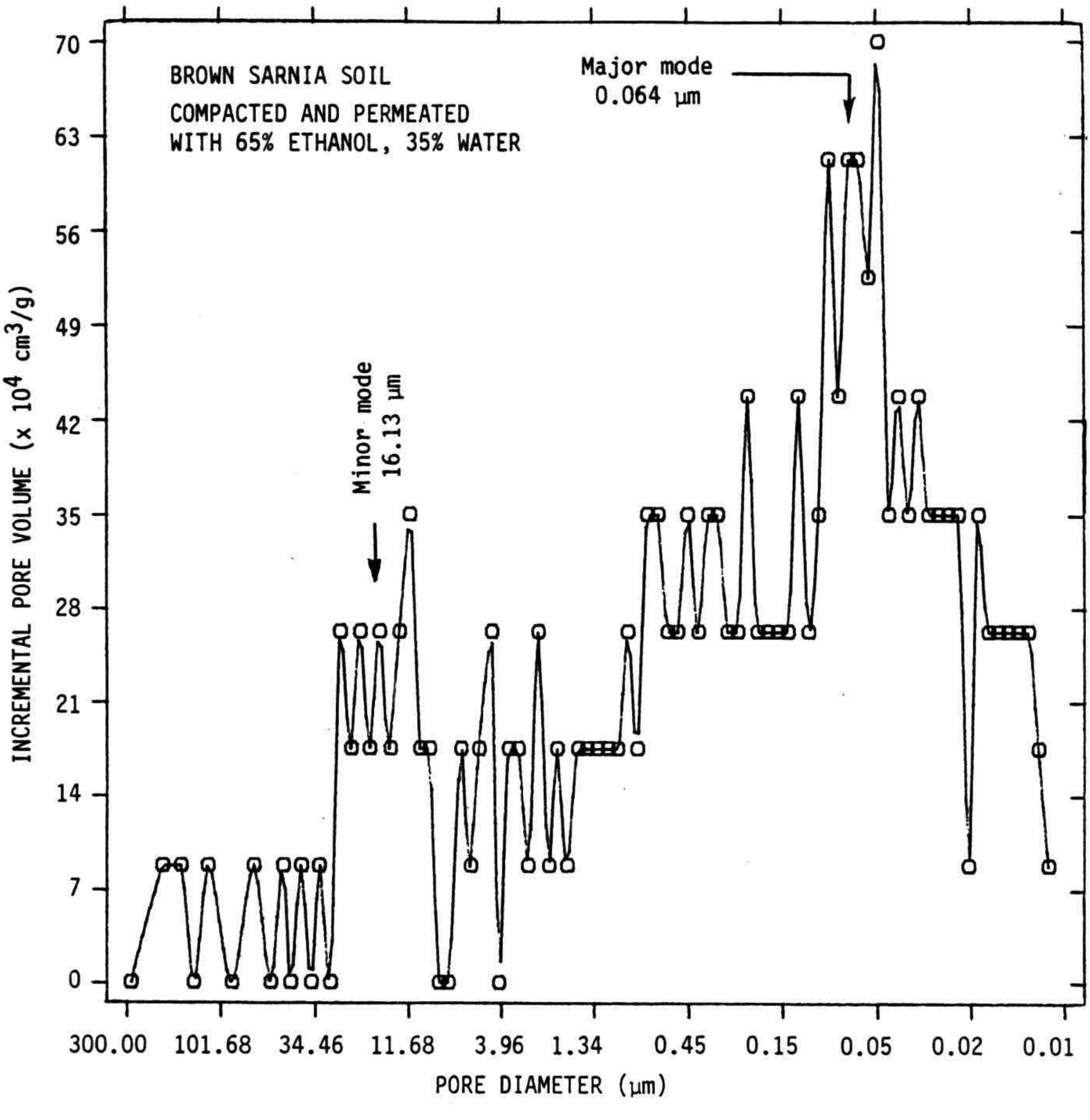


FIGURE 12. POST TESTING ASSESSMENT OF PORE SIZE DISTRIBUTION OF TEST SOILS MOULDED, COMPACTED AND PERMEATED WITH 65% ETHANOL AND 35% WATER

CONCLUSIONS

Although the work is still at a very preliminary stage due to unexpected interaction between the leachate and organic liquids, a few general conclusions may be drawn.

1. Raw leachate tends to flocculate on addition of alcohol producing semi-clear to clear supernatant liquids above "sinker" flocs. Addition of benzene with the alcohol caused the flocs to float.

2. Significant decreases in effluent salinity occur with the addition of alcohol.

3. Up to 50% alcohol added to leachate caused decreases in **k** primarily due to increased influent viscosity.

4. Moulding the clay in alcohol-bearing leachate is probably not a good idea since resultant flocculation appears to create large interped pores not as prominent in water moulded (dispersed) clays.

REFERENCES

Bowders, J.J., Daniel, D.E., Broderick, G.P. and Liljestrand, H.M., 1986. Methods for testing the compatibility of clay liners with landfill leachate. Hazardous and Industrial Solid Waste Testing: Fourth Symposium, ASTM STP 886, pp. 233-250.

Quigley, R.M. and Fernandez, F., 1985. Effects of increasing amounts of non-polar organic liquids in domestic waste leachate on the hydraulic conductivity of clay liners in southern Ontario. Proc. Technology Transfer Conference No. 6, Part 3, Liquid and Solid Waste Research, Ontario Ministry of the Environment, paper 46, pp. 244-264.

Daniel, D.E. and Liljestrand, H.M., 1984. Effects of landfill leachates on natural liner systems. Geotechnical Engineering Report GR 83-6, Geotechnical Engineering Center, University of Texas, Austin, 86 p.

APPENDIX A

TABLES OF LEACHATE COMPOSITION AND PROPERTIES

TABLE I. CHEMICAL COMPOSITION OF THE PRIMARY PERMEANT

Primary Permeant	Chemical Composition (% by weight)		
	Leachate	Ethanol	Benzene
1	100	0	0
2	80	20	0
3	60	40	0
4	40	50	10

TABLE II. CHEMICAL CONSTITUTION AND IONIC SPECIES CONCENTRATION OF THE SELECTED PERMEANTS

Selected Permeant	Chemical Constitution (% by wt.)			Ionic Species in Influent (g/L)					
	Leachate	Ethanol	Benzene	Sodium	Potassium	Calcium	Magnesium	Iron	Chloride
1	100	0	0	1.088	0.776	0.724	0.620	0.032	1.466
2	80	20	0	0.904	0.505	0.435	0.570	0.020	1.507
3	60	40	0	0.716	0.320	0.580	0.382	0.005	0.885
4	50	45	5	0.700	0.240	0.630	0.340	<0.001	1.005

TABLE III. VISCOSITY AND DENSITY OF THE SELECTED PERMEANTS

Selected Permeant	Density, ρ (g/cm^3)	Dynamic Viscosity, μ (centipoise)
1	1.0020	1.160
2	0.9704	2.091
3	0.9435	3.866
4	0.9312	2.822

TABLE IV. FLOC COMPOSITION

Permeant	Ionic Species (% by weight)					
	Sodium	Potassium	Calcium	Magnesium	Iron	Total
2	5	3.5	13.5	3.5	8	33.5
3	5	3.5	15	3.5	10	37
4	5	3	20	3.5	9	40.5

Evaluation of the impact of shock loading on the microbiota of the Welland River

By

Mike Dickman and Patricia Hayes
Department of Biological Sciences
Brock University
St. Catharines, Ontario, L2S 3A1

ABSTRACT

The specific conductivity of composite samples from two industrial discharges was compared to their continuous conductivity records. The composite samplers failed to adequately represent periods of shock loading. These shock loads were 2 to 3 times the average concentration of electrolytes in the industrial discharge.

It was concluded that composite samplers typically fail to reflect shock loading events and are therefore unacceptable instruments for monitoring temporal changes in industrial discharges to the environment where protecting the natural biota is the primary aim of the monitoring program.

The attached microbiota in rivers provide water managers and those entrusted with the protection of the organisms inhabiting our rivers with a built in continuous monitoring system. Waterways exposed to infrequent episodes of toxic effluent discharge (i. e. shock loading) will have a microbiota which is nearly as impoverished as the microbiota of continuously polluted waterways. Thus sporadic sampling of the water by water quality personnel and those employing composite samplers frequently fails to indicate the true water quality conditions in the area. The natural microbiota which serve as continuous monitors of water quality and continuous recording conductivity meters are far more reliable indicators of water quality than are composite samplers.

INTRODUCTION

In general, any rapidly increasing delta-type pulse which affects the chemical or physical environment of a natural area for a brief period of time can be classified as a shock load (Von Tumling 1968, Dickman 1973). When the species composition and diversity of attached algae are used to characterize the severity of an industry's discharge, a small volume polluter practicing shock loading will register an impact to the environment far greater than the volume and toxicity of its discharge would suggest. In some cases this impact will be equal to that of a large volume polluter which discharges continuously without shock loading (Dickman 1975). For example, in 1972-1974 the Canadian International Paper Company Ltd. (C.I.P.) pulp mill discharged annually approximately ten times the volume of the E. B. Eddy Co. Ltd. pulp mill. Nevertheless, the Ottawa River downstream of the E. B. Eddy Co. (during E.B. Eddy shock loading episodes) reached concentrations similar to those attained by C.I.P. during its normal loading conditions (Dickman 1975). Even though these shock loads from the E. B. Eddy Co. were infrequent, the attached algal community downstream of that company was as impoverished as the one downstream of C.I.P. (Ibid.). Thus it was concluded that the sporadic dumping by the E. B. Eddy Co. was as detrimental to the downstream microbiota as the continuous dumping of a much larger volume of effluent by C.I.P.

The significance of this conclusion is important to environmental agencies entrusted with monitoring the effects of industrial discharges on the natural biota of our lakes and streams. To date, most Canadian environmental agencies and industries have persisted in collecting composite samples rather than continuous samples (Dalrymple 1985). Composite samplers such as the ones used by the Ontario Ministry of the Environment fail to reveal peaks or shock loading events.

In this paper, we will examine the consequences of using a continuous recorder in place of a composite bucket-type sequential sampler as a means of gauging water quality conditions in terms of electrolytic shock loading. It must be emphasized that the primary focus of this study was directed toward the analysis and the protection of the natural biota of the wetlands portion of the lower Welland River where it flows into the Niagara River (Figure 1) and thus to Lake Ontario. It is recognized that all substances borne by the Welland River impact directly on the Niagara River and Lake Ontario (Dickman et al., 1983; Kaiser et al., 1983; Comba & Kaiser, 1984).

METHODS

Specific conductivity meters respond to the concentration of electrolytes in the water. A continuous recording Model SI-1 Lisle Specific Conductivity meter was installed below the Cyanamid Canada Inc. Chemical Company near the confluence of Thompson's Creek (Fig. 1, Station No. 4). Concomitantly, a YSI Instruments Co. battery operated specific conductivity meter was employed upstream at Station No. 3. The two instruments were intercalibrated and cross checked at daily intervals. The same technique was also adopted at Stations 1 and 2 above and below the Atlas-Mansfield outfall (Fig. 1). Peaks in specific conductivity below these two outfalls which did not occur upstream were assumed to result from shock loading discharges of electrolyte containing effluents. Both Atlas Steels and the Diversitech General Company discharge into the Altas-Mansfield sewer while the Cyanamid Chemical Company is the only industry discharging large volumes of material into Thompson's Creek. The dates for monitoring the effluent being discharged into the Welland River by each of these industries were chosen at random. Attached algae (periphyton) from above and below these Welland River sites was removed by scraping an area of approximately 1 cm^2 using standard procedures (Wetzel 1964). Epipelic samples were taken by removing only the top 1-2 mm of the sediment on top of the mud. All epipelic replicate samples from each area were pooled and then homogenized. A 1 ml subsample was suspended in 10 ml of filtered tap water and placed in a sedimentation chamber with a few drops of Lugol's solution (Wetzel 1964). After sedimentation was complete (24 hr), the chamber was placed on a Leitz orthoplan inverted microscope stage and the microbiota enumerated by selecting 10 ocular fields at 150 X, 600 X and 1,500 X magnifications. Epiphytic samples were taken whenever Typha (cattails) or Phragmites (bullrushes) were present. An area of 1 cm^2 was scraped from near the waterline for each of three stems of these emergent aquatic macrophytes. These scraping samples were then pooled and analyzed as described above for the epipelic samples.

Counting procedures for the microbiota were similar to those described by Andrews and Lohmann (1972). Category one (rare taxa = 1-10 individuals per slide) was represented by the number 10, category two (10-200 individuals/slide) was represented by the number 200 etc. This procedure of presenting quantitative data as ranges (rare = 1-10 individuals per slide, 2 = moderate = 10-200 individuals per slide, 3 = common = 200 - 3,000 individuals per slide, and 4 = abundant = 3,000-40,000 individuals per slide) has been adopted by numerous scientists. Rounding off the number of significant figures to avoid indicating more precision than the data warrant is also recommended (Koivo and Ritchie 1978).

RESULTS

We monitored the Cyanamid discharge at station 4 on Thompson Creek (Fig. 1) on March 4, 1986 with our Lisle continuous conductivity meter. We then reviewed the data on the strip chart recorder and calculated what a one litre bucket type sequential composite sample taken every 15 minutes would represent in terms of its 12 hour composite sample (Table 1). During the same 12 hr. period the specific conductivity meter registered two shock loads with peaks of 2,150 and 1,780 microsiemens/cms (Fig. 2). The specific conductivity from the bucket sampler composite sample was calculated for purposes of comparision (920 microSiemens/cm).

The specific conductivity recorded at the Atlas-Mansfield outfall (Sites 1 & 2, Fig. 1) showed seven spikes (shock loads) during a 12 hr. period ranging from a low of 1,500 microSiemens/cm to a high of 5,000 microSiemens/cm (Fig. 2). Subsequent to this study which took place in June and July of 1986, the Atlas Specialty Steels Division shut down its Welland Plant in order to remedy this shock loading problem. In September and October, their discharge was again monitored and we concluded that over 80% of the shock loads had been eliminated by the remedial action taken by the Atlas Specialty Steels Division, Welland Plant.

Although the 12 hr mean conductivity at the Atlas-Mansfield outfall was only slightly higher than Cyanamid's, 12 hr mean (1,149 vs 920 microSiemens/cm) the peaks in the Atlas-Mansfield outfall conductivity record were far higher (5,000 vs. 2,150 microSiemens/cm), and far more frequent. The relationship this bears to the downstream microbiota is represented in Tables III and IV. The biotic diversity and species richness below both outfalls was compiled (Table V) from the data provided in Tables III and IV.

When the biotic diversity as reflected by both the Shannon-Weiner and Simpson diversity indices was regressed against distance downstream below the two outfalls, a significant ($p < 0.01$) correlation coefficient resulted (Table V).

DISCUSSION

Floristic Zonation Pattern

The distribution of higher aquatic plants below industrial outfalls was used as the basis for defining a zonation pattern to characterize the size of the impact and recovery zones below industries discharging toxic wastes into the Welland River (Dickman et al 1980). Immediately below a toxic waste outfall, a zone was encountered in which all higher aquatic plants were absent (impact zone; zone 1). Below the impact zone, three contiguous recovery zones were identified. The primary recovery zone (Zone 2) was characterized by tall emergent higher aquatic plants (HAP) (eg. Typha and Phragmites). The secondary recovery zone (Zone 3) was characterized by short HAP's (eg. Pontederia, Sagittaria and Sparganium as well as floating leaved HAP's (eg. Potamogeton, Nuphar and Nymphea). In addition, aquatic plants already noted for zone 2 were also present in zone 3. The tertiary recovery zone (Zone 4) was characterized by the presence for the first time of submersed HAP's (eg. Elodea, Ceratophyllum and Myriophyllum). A schematic representation of these 4 zones is provided (Fig. 3).

The relationship between the size of each of these zones and the toxicity and volume of effluents being discharged into it is the subject of an ongoing research program at Brock University. In general, the more toxic the effluent, the larger the size of the impact or dead zone below the discharge pipe. This relationship holds true regardless of whether the effluent is discharged continuously or sporadically.

Atlas-Mansfield Discharge

The effluent entering the Welland River at the Atlas-Mansfield sewer outfall was composed primarily of iron oxides and heavy metals. During periods of overflow, Atlas Steel's north and south waste treatment plant effluents, plus Diversitech's effluent, yard runoff and stormwater from the McAlpine municipal sewer was discharged into the Atlas-Mansfield Sewer (Dalrymple 1985 and Lindall Pers. Comm.). Atlas Specialty Steels, a division of Rio Algom Ltd., manufactures stainless steel alloys, dies, mold-blocks and die steel at its Welland River Plant. The raw materials for this production consists primarily of steel scrap, lime, ferrochrome, nickel oxide and ferro silicon (Ibid). Diversitech General Engineered Elastomers Division in Welland manufactures custom rubber compounds, mold bonded products, dense and sponge molded rubber, track bars and vibration isolation bushings.

The flow rate at the outfall of the Atlas-Mansfield sewer into the Welland River is approximately 30,000 m^3/day (Dalrymple 1985). Atlas Steels is a known source of chromium, iron, lead, nickel and zinc as well as phosphorus, nitrogen, sulphate, C.O.D., dissolved and suspended solids (Ibid). Diversitech is a known source of various rubber and plastic precursors. In April and May of 1986, oily wastes coated much of the downstream vegetation below the Atlas-Mansfield outfall. Other organic contaminants such as di and trichloroethylene were found only at trace levels by the Ministry of the Environment. Phenols were significantly higher at the Atlas 42" sewer manhole than in the Atlas intake water (Dalrymple 1985). As a result of these discharges a dead zone (zone 1) is associated with the outflow area of the Atlas-Mansfield storm sewer.

The first higher aquatic plant (Phragmites communis) which we encountered was located approximately 20 m below the Atlas-Mansfield Sewer outfall. Microflagellates, both heterotrophic forms (unpigmented colorless taxa, e.g. Sarcodina) and flagellated autotrophs (pigmented taxa) dominated the microbiota at this site (Table III). As one moved progressively further downstream into the secondary and tertiary recovery zones, the total number of species increased to 19 and the ratio of autotrophs to heterotrophs (ciliates, rhizopods and colourless flagellates) significantly increased ($P < 0.01$) over the same distance (Table III).

Cyanamid Impact

The Cyanamid Canada Inc. Welland River Plant has several outfalls to Thompson's Creek which carries their wastes into the Welland River approximately 4.5 km upstream of the Niagara River at Queenston (Fig. 1). Cyanamid manufactures a wide variety of nitrogen and phosphorus based chemical products including ammonia, urea, nitric acid, dicyandiamide, xanthate, cyphos animal feed, phosphates, guanidine, tetrabutyl-phosphonium pesticides and phosphine (Dalrymple 1985 and Draper, Pers. Comm.). The average flow from Cyanamid in 1981 was 19,200 m^3/day (1982 M.O.E. Data reported by Dalrymple 1985). On average, this 1981 daily discharge contained 184 kg phosphorus, 9,370 kg ammonia and urea nitrogen, 5,210 kg nitrate nitrogen, 5.57 kg free cyanide, 4.86 kg chromium, 1.78 kg nickel, 2.97 kg zinc and .113, .008, .064, .019, .008 kg of total phenols, arsenic, toluene, chloroform and naphthalene respectively (1981 EPS Data reported by Dalrymple 1985). Immediately downstream of the Cyanamid discharge pipes there is a dead zone in which no higher aquatic plants are able to survive. This dead zone (zone 1) extends from the Cyanamid discharge to Thompson's Creek for over 2 Km and on into the Welland River for a distance of 75 m along its north shore.

The large discharge of nitrogen-rich substances from Thompson's Creek into the Welland River at Station 4 has consistently stimulated the production of high numbers of the pollution tolerant flagellate, Euglena convoluta in the impact zone (Table IV, Dickman et al 1983). The number of heterotrophs and autotrophs were equal in the impact zone (8 taxa of each) and gradually the number of autotrophs increased downstream as the number of heterotrophs fell from 8 to 4 by the time the secondary recovery zone was reached. Total species richness increased from 16 taxa in the impact zone to 19 in the tertiary recovery zone (Table V). The Simpson Index increased from 0.48 in Zone 1 to 0.74 in Zones 4 and 5. The Shannon-Weiner Diversity index increased proportionately (Table V).

Shock Loading

The relationship between the biotic zonation pattern below an industrial outfall and the toxicity of that industry's discharge is complicated by the fact that few industries discharge their toxic wastes in a continuous fashion. Shock loading is the rule rather than the exception (Dickman 1975). When a large dead zone and a large recovery zone is discovered downstream of an effluent pipe that is not discharging a toxic waste, the possibility of shock loading should be investigated. To this end a continuous monitor rather than a composite sampler is recommended.

In conclusion, continuous monitoring and the use of natural in-stream biological monitors should replace sporadic spot samples and composite sampling in all water quality programs which have as their primary goal, the protection of the natural biota of our lakes and rivers. Where pont source discharges contain electrolytes, continuous specific conductivity monitoring permits a better understanding of the resulting downstream distribution of microbiota and higher aquatic plants. If a continuous conductivity recorder was coupled to a composite sampler so that samples were taken only during periods of shock loading, we feel that the analysis of these samples would improve our ability to interpret the distribution of the biotic assemblages located downstream of industrial outfalls.

ACKNOWLEDGEMENTS

This research has been supported by grants from the Ontario Ministry of the Environment and the World Wildlife Toxicology Program. We are also grateful to members of the Employment and Immigration, Fisheries and Oceans toxicology team, Dave Neufeld, Bill Parkins and Robert Steele for collecting the specific conductivity data and to Barbara Hamilton and Marilyn Ferracuti for typing this manuscript.

REFERENCES CITED

Andrews, R. and K. E. Lohmann, 1972. A proceedings for the microscopical study of diatomaceous sediments. Proceedings of the Beiheft Zur Nova Hedwigia Bremerhaven. 39: 267-281

Cairns, J. C., Lanza, G. R. and Parker, B. C. 1972. Pollution related structural and functional changes in aquatic communities with emphasis on freshwater algae and protozoa. In Proc. Acad. Nat. Sci. Philadelphia Vol. 124: 79-127

Comba, M. E., and K. Kaiser, 1984. Tracking River Plumes with volatile halocarbon contaminants: the Niagara River - Lake Ontario example. J. Great Lakes Research 10:375-382.

Dalrymple, R. J. 1985. Canadian Point Sources to the Niagara River. Final report on M.O.E. and E.P.S. 1981/82 surveys. NRTC Appendix report, Ontario Ministry of the Environment, Niagara River Improvement Project. Rexdale, Ontario, 157 pp.

Dickman, M. 1973. Total dissolved electrolyte effects on periphyton. J. Water Pollution Control Federation 45: 2211-2215

Dickman, M. 1975. A comparison between the effects of sporadic and continuous loading from sulphite paper mills on attached algae in the Ottawa River near Ottawa, Canada. Proc. Water Pollution Research 10: 65-72

Dickman, M., J. Smol and P. Steele 1980. The impact of industrial shock loading on selected biocoenoses in the lower Welland River, Ontario. Water Pollution Research Journal of Canada 15: 17-31

Dickman, M., C. Prescott and K. L. E. Kaiser. 1983. Variations in the aquatic vegetation of the Welland River (Ontario, Canada) above and below an industrial waste discharge. J. Great Lakes Research 9: 317-325

Kaiser, K., M. Comba, and H. Huneault. 1983. Volatile halocarbon contaminants in the Niagara River and in Lake Ontario. J. Great Lakes Research 9: 212-223.

Koivo, L. K. and J. C. Ritchie. 1978. Modern diatom assemblages from lake sediments in the boreal-arctic transition region near the Mackenzie Delta, N.W.T. Canada. Can. J. Bot. 56: 1010-1020

Moore, J. W. 1979. Diversity and indicator species as measures of water pollution in a subarctic lake. Hydrobiologia 66: 73-80

Patrick, Ruth. 1949. A proposed biological measure of stream conditions, based on a survey of the Conestoga Basin, Lancaster County, Pennsylvania. Proc. Acad. Nat. Sci. Philadelphia, 101: 277-341.

Thienemann, A. 1939. Grundzuge einer allgemeinen Okologie. Arch. I. Hydrobiol., 35: 267-285.

Von Tumling, W. 1969. Suggested classification of water quality based on biological characteristics. 4th Int. Conf. Water Poll. Res. pp. 40-42, Pergamon Press, Oxford

Wetzel, R. G. 1964. A comparative study of the primary productivity of higher aquatic plants, periphyton and phytoplankton in a large, shallow lake. Int. Rev. Ges. Hydrobiol. 49: 1-64

Table Captions

Table I	Continuous recording specific conductivity quarterly hour values of the conductivity of the water in Thompson's Creek near its confluence with the Welland River (4 March 1986, 12 noon to 12 midnight).
Table II	Continuous recording specific conductivity quarterly hour values of the water in the Atlas-Mansfield sewer at its confluence with the Welland River (25 March 1986, 12 noon to 12 midnight).
Table III	The commoner algae and microheterotrophs scraped from the mud (Zone 1) and *Phragmites communis* stems (Zones 2-5) near the outfall of the Atlas-Mansfield outfall.
Table IV	The commoner algae and microheterotrophs scraped from the mud (Zone 1) and *Typha latifolia* stems (Zones 2-5) near the confluence of Thompson's Creek and the Welland River.
Table V	Microbiotic species richness and Shannon-Weiner and Simpson diversity indices in each of the zones above and below the Cyanamid and the Atlas-Mansfield outfalls to the Welland River. The Shannon-Weiner diversity (Y) was regressed against the zone location number for each of the five zones (X axis) to provide the summary data set at the bottom of the table.

TABLE I (Cyanamid)

Time of Day	Conductivity	Time of Day	Conductivity
12 noon =	1,000 (µS/em)	6:15 =	1,000 (µS/cm)
12:15	900	6:30	900
12:30	900	6:45	900
12:45	1,000	7:00	900
1:00	900	7:15	900
1:15	900	7:30	900
1:30	900	7:45	900
1:45	1,000	8:00	900
2:00	1,000	8:15	900
2:15	1,000	8:30	900
2:30	1,000	8:45	800
2:45	1,000	9:00	800
3:00	1,000	9:15	800
3:15	1,000	9:30	800
3:30	900	9:45	900
3:45	900	10:00	800
4:00	900	10:15	800
4:15	900	10:30	800
4:30	900	10:45	800
4:45	900	11:00	800
5:00	900	11:15	800
5:15	900	11:30	1,300
5:30	900	11:45	1,500
5:45	900	12:00 mid.	800
6:00	1,800		

Mean conductivity = 920 µS/cm for 49 samples. The 2 peaks in conductivity during the same period were 2,150 and 1,780 µS/cm.

TABLE II (Atlas Mansfield)

Time of Day	Conductivity	Time of Day	Conductivity
12 noon =	1,800 (μS/cm)	6:15 =	1,400 (μS/cm)
12:15	1,800	6:30	2,400
12:30	1,300	6:45	600
12:45	3,000	7:00	1,500
1:00	2,000	7:15	900
1:15	1,900	7:30	700
1:30	1,500	7:45	900
1:45	1,800	8:00	400
2:00	2,500	8:15	1,200
2:15	1,700	8:30	900
2:30	1,000	8:45	700
2:45	1,200	9:00	600
3:00	2,100	9:15	800
3:15	2,000	9:30	600
3:30	1,900	9:45	1,500
3:45	800	10:00	800
4:00	600	10:15	600
4:15	500	10:30	900
4:30	500	10:45	800
4:45	500	11:00	900
5:00	500	11:15	800
5:15	2,100	11:30	900
5:30	2,000	11:45	700
5:45	1,500	12:00 mid.	900
6:00	2,200		

Mean conductivity = 1,149 μS/cm for 49 samples. 7 peaks during this same period were 4,200, 4,500, 4,900, 5,000, 3,400, 4,000 & 3,00 μS/cm.

TABLE III

	Upstream of* Atlas-Mansfield Outfall Zone 5 200m	** Impact Zone Zone 1 0-20m	Primary* Recovery Zone Zone 2 20-200m	Secondary* Recovery Zone Zone 3 200-400m	Tertiary* Recovery Zone Zone 4 400m-1 km
CHLOROPHYTA					
FILAMENTOUS GREEN ALGAE					
Zygmena	1				1
NON-FILAMENTOUS GREEN ALGAE					
Ankistrodesmus falcatus	3		1	1	2
microflagellates	3		3	4	2
EUGLENOPHYTA					
Euglena convoluta				1	
BLUE GREEN ALGAE (CYANOPHYCEAE)					
Chroococcus sp.	2				1
Oscillatoria sp.	2			4	3
Spirulina cf Nordstedii	3				3
Rhabdoderma sp.	3				2
BACILLARIOPHYTA					
Achnanthes sp.	1		1	1	1
Cocconeis sp.	1				1
Fragilaria crotonensis				4	2
Gomphonema angustatum				3	3
Navicula sp.	2		2	1	2
Nitzschia palea		1	1	1	
Nitzschia sp.	2		1	2	1
Pinnularia sp.					1
Stauroneis smithii					1
Surirella sp.	1			2	1
CILIOPHORA					
Colpidium	1				
Opistotricha	1				
Tetrahymena	3				
Trinema cf compressum	1				
RHIZOPODA					
Colorless Rhizopoda <5	1		2	2	3
SARCODINA					
Colorless microflagellates <5	3	1	3	2	1

* Epiphytic taxa growing on Phragmites
** Epipelic taxa only

TABLE IV

Species Name	* Upstream of Cyanamid 200m	** Zone 1 impact zone 20m	** Zone 2 20-200m	** Zone 3 200-1,000m	** Zone 4 1-2 km
CHLOROPHYTA					
microflagellates (<5 µm)	3	1	2	3	3
FILAMENTOUS GREEN ALGAE					
Mougeotia sp.	2			1	2
Ulothrix sp.	2	1	1	1	2
EUGLENOPHYTA					
Euglena convoluta	1	4	2	2	1
BLUE-GREEN ALGAE (cyanophyceae)					
Oscillatoria sp.	2	2	2	2	1
BACILLARIOPHYTA					
Achnanthes sp.	1			1	1
Gomphonema sp.	1	2	2	1	1
Gyrosigma sp.				1	
Navicula sp.	3	3	3	3	2
Nitzschia sp. 1	2	2	2	3	2
Nitzschia palea	2	3	2	2	3
Nitzchia sp. 2	1			1	2
Pinnularia sp.	3		2	3	3
Stauroneis smithii	1				1
Surirella sp.	1			1	1
Tabellaria fenestrata	1				
PYRROPHYTA					
Glenodinium sp.	1	3		1	
CILIOPHORA					
Colpidium sp.		1	1		
Colpoda sp.		2	1	1	1
Opisthotricha sp.	1	1	2	2	2
RHIZOPODA					
Colorless amoebae	1	2	2		1
SARCODINA					
Monas	2	3	2	1	1
Colorless Monoflagellates <15 µm		1	1		1
BACTERIA					
Bacteria	1	3	3-4	1	1

* Epiphytic taxa growing on Typha

** Epipelic taxa only

TABLE V

	Cyanamid - Outfall			Atlas-Mansfield Outfall		
	Species Richness	Shannon Diversity	Simpson Diversity	Species Richness	Shannon Diversity	Simpson Diversity
Zone 1	16	1.6	0.48	2	1.0	0.53
Zone 2	16	1.8	0.54	8	1.4	0.56
Zone 3	19	2.3	0.73	14	1.9	0.69
Zone 4	20	2.3	0.74	18	2.5	0.79
Zone 5 (upstream station)	20	2.3	0.74	18	2.9	0.85

```
Summary data for:  X *        Y *

Sample Size (N):   5          5  ***
  Sums:           15         10.3
  Means:           3          2.06
  Sum of Squares: 10           .452
  Sum of Sq. YX:         1.9
  Variance Y on X:       .0303333333
  Slope:                 .19
  S.E. of Slope:         .0550757054
  T for Slope=0(3 DF) 3.44979694
  Y-Intercept:           1.49
  Proportion of Y-Var
  due to X (R-squared) .798672567
  Bi-variate Normal
  Corr. Coefficient (R).893684825
```

```
Summary data for:  X **   Y **

Sample Size (N):   5      5   ***
  Sums:           15      9.7
  Means:           3      1.94
  Sum of Squares: 10      2.412
  Sum of Sq. YX:       4.90000001
  Variance Y on X:     3.66666579E-03
  Slope:                 .49
  S.E. of Slope:         .0191485399
  T for Slope=0(3 DF)25.5894185
  Y-Intercept:           .47
  Proportion of Y-Var
  due to X (R-squared) .995439471
  Bi-variate Normal
  Corr. Coefficient (R).997717129
```

* where X = Cyanamid Zones 1-5 and Y = Shannon Diversity indices (Log base 2)

** where X = Atlas-Mansfield Zones 1-5 and Y = Shannon Diversity indices (Log base 2)

*** All diversity calculations were made on the basis of total biomass per taxon rather than total numbers per taxon.

Figure Captions

Figure 1 The Welland River study area detailing the location of zone 5 upstream of the Atlas-Mansfield outfall (No. 1) and Zones 1-4 (No. 2) downstream of the same as well as zone 5 upstream of the Cyanamid Chemical Company (No. 3) and zones 1-4 below the confluence of Thompson's Creek. The inset represents the location of the study area in the Niagara Peninsula.

Figure 2 Evidence of shock loading to Thompson's Creek (upper figure) and to the Atlas-Mansfield sewer (lower figure) based on continuous 24 hr specific conductivity data for these two locations.

Figure 3 Schematic representation of the higher aquatic plant zonation pattern above and below a toxic outfall.

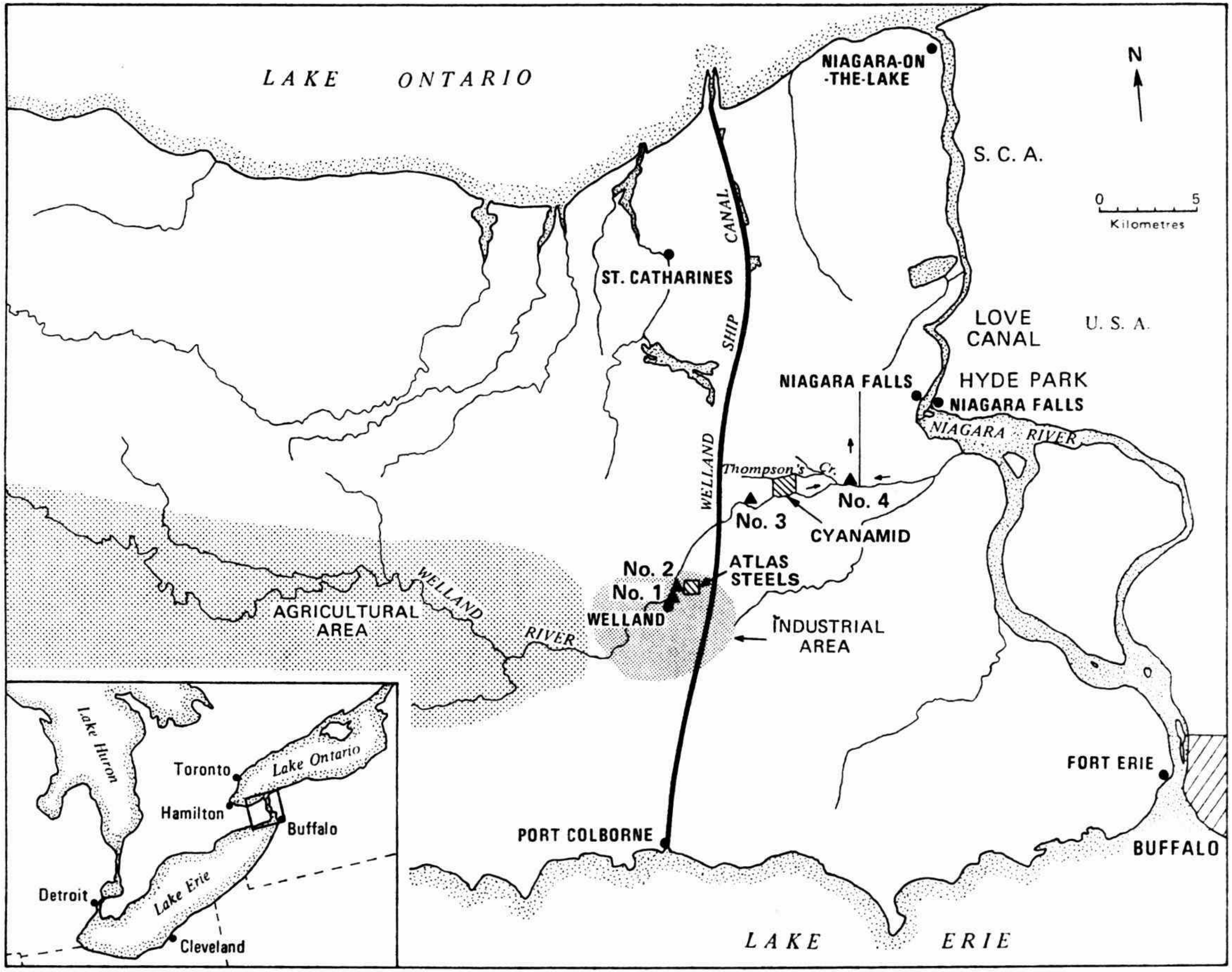
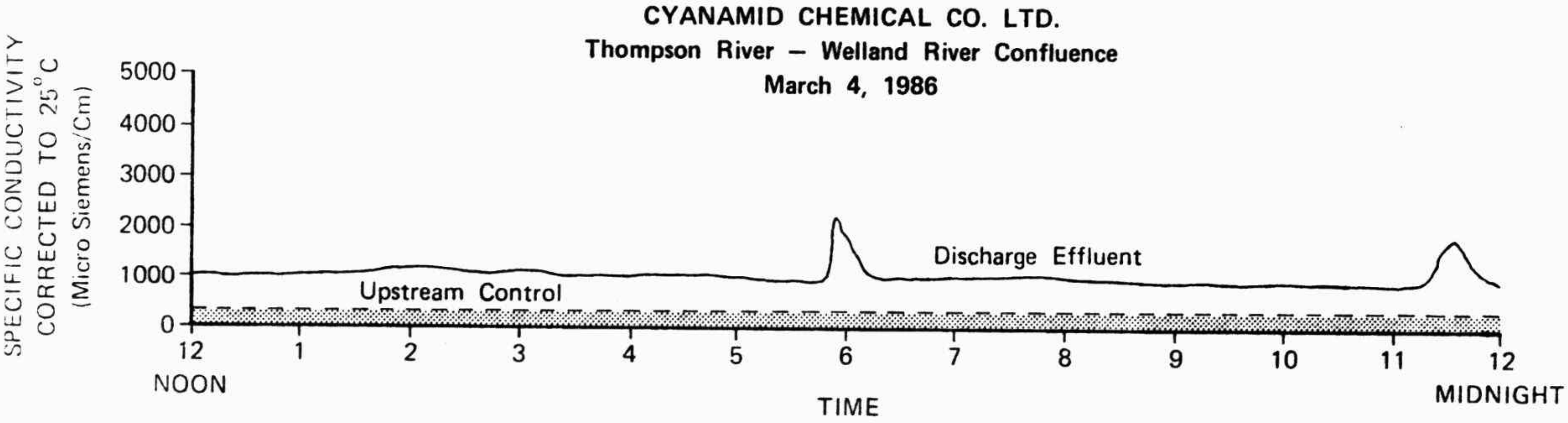

LAKE ONTARIO
NIAGARA-ON-THE-LAKE
N
S. C. A.
0 5
Kilometres
ST. CATHARINES
WELLAND SHIP CANAL
LOVE CANAL
U. S. A.
NIAGARA FALLS
HYDE PARK
NIAGARA FALLS
NIAGARA RIVER
Thompson's Cr.
No. 3
No. 4
CYANAMID
No. 2
No. 1
ATLAS STEELS
WELLAND
AGRICULTURAL AREA
WELLAND RIVER
INDUSTRIAL AREA
Lake Huron
Lake Ontario
Toronto
Hamilton
Buffalo
Detroit
Lake Erie
Cleveland
FORT ERIE
PORT COLBORNE
BUFFALO
LAKE ERIE

Fig. 1

Fig. 2

CONTINUOUS CONDUCTIVITY SERIES


CYANAMID CHEMICAL CO. LTD.
Thompson River – Welland River Confluence
March 4, 1986

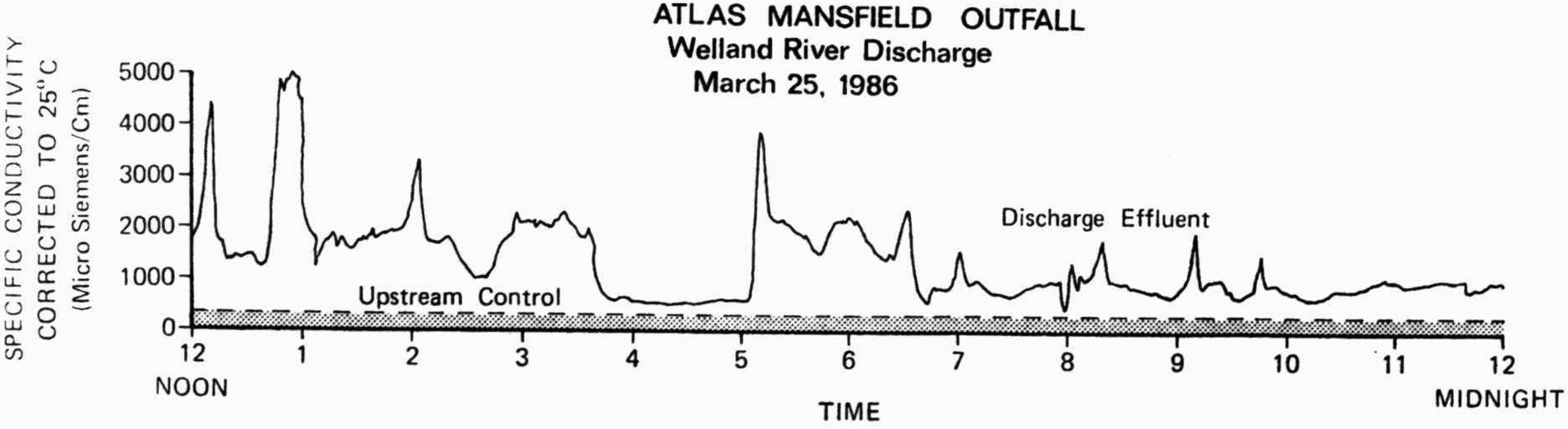
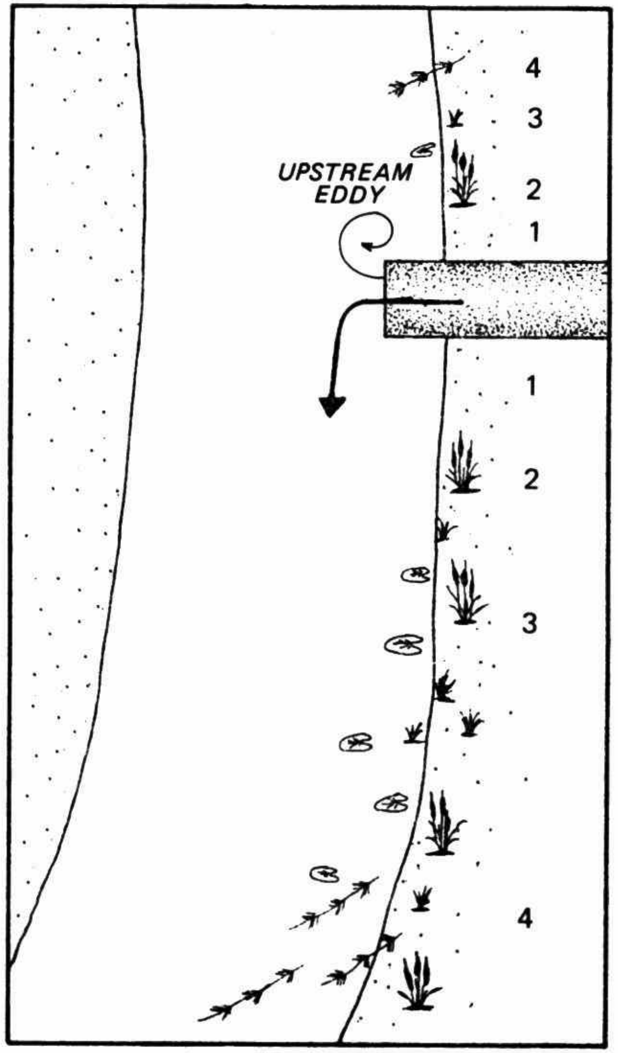

ATLAS MANSFIELD OUTFALL
Welland River Discharge
March 25, 1986

FIGURE 3 IDEALIZED ZONATION PATTERNS

KEY

1 IMPACT ZONE
2 PRIMARY RECOVERY ZONE
3 SECONDARY RECOVERY ZONE
4 TERTIARY RECOVERY ZONE



RIVER

EVALUATION OF CONTAMINANT VELOCITY IN LOW-PERMEABILITY FRACTURED SHALE

R. Blackport
E.A. Sudicky
J.A. Cherry

Institute for Groundwater Research
University of Waterloo
Waterloo, Ontario
N2L 3G1

Introduction

Knowledge regarding the subsurface migration of toxic contaminants from waste disposal or industrial sites in shale areas has become important in much of the heartland of the heavily-industrialized regions of southern Ontario. In the Oakville-Mississauga region, the Dundas shale is not far beneath ground surface. The Burlington-Hamilton region has the Queenston and Rochester shales and the Niagara Falls region has various shales including the Queenston shale at waste disposal and industrial sites; in the Niagara Falls region the Queenston shale lies beneath other rock units but it is an important hydrogeologic zone that may transmit contaminants through to the Niagara River.

One of the most important steps in the prediction of the extent to which groundwater contamination will occur at municipal landfills and at other waste disposal sites is the determination of the average velocity of non-reactive contaminant migration in groundwater. In our investigations of groundwater contamination, we have found that the greatest difficulties and uncertainties in contaminant velocity measurements and predictions occur at sites on fractured bedrock. For example, hydrogeologic investigations performed on the Queenston shale at Bayview Park landfill site have shown that this shale has a relatively low apparent hydraulic conductivity (i.e. low permeability) except at very shallow depth where weathering is an obvious cause of higher permeability. This finding of generally low permeability is consistent with previous studies of this shale in the Burlington-Hamilton area. Our investigations of the Bayview Park site have also shown, although not in an entirely conclusive manner, that the velocity of migration of non-reactive contaminants in this low-permeability shale is relatively large. This leads to the expectation that very large contaminant plumes can develop in fractured shale under conditions of relatively low contaminant mass flux through the shale.

If our preliminary finding of relatively large horizontal contaminant velocities in the Queenston shale is correct, it is reasonable to expect that landfills situated on fractured shale can produce large plumes of groundwater contamination that extend over considerable distances from the contaminant source. Our objectives, therefore, are (i) to apply and evaluate various methods for velocity determination in low-permeability zones in the shale, (ii) to determine whether or not our preliminary finding of large horizontal contaminant velocity in the shale is correct, and (iii) to assess the degree to which diffusion of contaminants from the fractures in the porous rock matrix can attenuate rapid advection along the fractures.

Study Site

A site on Petro-Canada property in Clarkson, Ontario was selected and a preliminary phase of drilling and instrumentation has been performed. The site was chosen for several reasons. It is located on the Dundas shale, a moderate- to low-permeability fractured shale hydrogeologically similar to other shale deposits in Southern Ontario. General background hydrogeological information was available indicating a shallow water table, thin overburden (2 metres), and flay lying bedrock. The site has easy access and is a secure site with respect to long-term monitoring and limited potential for vandalism.

A preliminary drilling program conducted in May, 1986 utilized a track mounted CME750 drill rig from the University of Waterloo. Five boreholes were continuously cored using an NV3 core barrel. The boreholes were placed 15 metres apart in two perpendicular rows of three.

Each borehole was drilled in the following manner. Hollow stem augers were advanced until refusal in the weathered bedrock at approximately 3 metres depth. The borehole was then drilled by triconing to a depth of approximately 5.5 metres. This was done because the upper weathered bedrock had a number of clay zones causing problems with water circulation during coring of the first borehole. Boreholes were cored from approximately 5.5 metres to 16.5 metres below ground surface at each location.

Results of rock coring indicate that the majority of the rock is a shale with some layers of dolomite within the shale. The dolomite zones are generally 5-20 cm thick. The fracture pattern is primarily horizontal in the shale and vertical in the dolomite. Many of the dolomite zones had broken shale above and below; however, it was difficult to determine if this was induced by drilling.

The degree of fracturing generally decreased with depth as the RQD ranged from 50% in the upper bedrock to 80-85% in the lower part of the borehole. Fractures were generally along bedding planes and were usually tight. Some vertical fractures in the dolomite had precipitation of either marcasite or pyrite indicating water movement through these fractures.

The rock core was logged in the field and photographed in 60 cm sections. Several fracture zones were encountered during drilling of each borehole. The location of these main fracture zones were correlated between each borehole using the field logs and photographs of the core to determine which fracture zones could be continuous across the site. The main fracture zones encountered which showed the potential for continuity across the site were at depths 6.5-6.8 metres, 7.2-7.6 metres, 10.4-10.7 metres and 14.0-14.3 metres below ground. Many of these zones contained dolomite beds.

Instrumentation and Hydraulic Response Tests

Once the drilling was completed, casing was installed in the upper 5 metres of the borehole and the borehole left open to allow for downhole testing. The first testing conducted was pressure-packer permeability testing of the main fracture zones encountered to estimate the permeability of these zones and also determine if the fracture zones were very localized.

The fracture zones were isolated using a double packer assembly which was pneumatically inflated with nitrogen. Water was then injected into the isolated zone at a constant pressure and flow rate. The water was injected from a series of interconnected reservoirs of various diameters (1.25 cm - 6.5 cm) to allow for better calibration at low flow rates (i.e. if the test zone was tight than a small diameter reservoir was used and if the test zone was quite permeable than all the reservoirs were used).

General results of packer testing indicated that the zone of highest permeability (on the order of 5×10^{-4} to 1×10^{-4} cm/s) is located at depths between 10.4-10.7 metres. Because the actual zone tested was 1.2 metres in length, this range in hydraulic conductivity values can only be regarded as a bulk estimate for the fracture zone. Additional testing of a more localized nature (smaller test intervals) is being performed to determine if this zone is suitable for a natural-gradient tracer test to directly assess contaminant flux rates.

Other zones tested had a lower permeability, but many of these tests exhibited a decrease in a rate of flow of injected water as the test continued. This decrease occurred for each increase in injection pressure and would appear to indicate that many of these fracture zones were localized and not continuous in lateral extent. In this case, the permeability of the matrix becomes the controlling factor for water movement. The rock zone above and below the most permeable fracture zone (10.4-10.7 metres below ground) was packer tested in several of the boreholes and the permeability was estimated to be less than 10^{-7} cm/sec.

Several double-packer systems were constructed to isolate the main fracture zone at two boreholes with the standard pressure packer system being used at a third borehole to isolate and pump the main fracture zone. A short-term pumping test was then performed to determine if this fracture zone is well connected and if so, aid in the design of a long-term pumping test utilizing a multilevel packer system situated in all boreholes.

Results of the short term pumping test indicate that a hydraulic connection exists between at least four of the five observation wells. The test zone was pumped at approximately 1.5 L/min.

A multilevel double-packer system has been constructed and installed in each borehole to isolate discrete zones for detailed response testing and to allow routine water-level monitoring within each zone. Up to five discrete zones can be isolated with this packer system. The system contains a series of packers which are inflated pneumatically and have holes drilled and threaded through the upper and lower bulkheads of each to connect tubing from each zone up to ground surface. The length of each of the five test intervals can be varied with this monitoring device as well as the depth of placement.

Use of the multilevel monitoring devices permit estimation of detailed permeability profiles by single-well hydraulic responses and borehole dilution testing. In addition, such devices allow determination of the degree of fracture interconnectivity between boreholes when one of the zones is pumped continuously. Work of this nature is currently in progress.

Velocity Determination

The following methods are being implemented to estimate the groundwater velocity in the fractured shale at the test site.

1. calculations based on Darcy's law and measured values of hydraulic conductivity, hydraulic gradient and estimates of effective fracture porosity
2. the borehole dilution test method (i.e. a single-borehole tracer test method)
3. natural-gradient and forced advection tracer tests (i.e. tracer tests using many multilevel devices for tracer monitoring).

Darcy's law for velocity determination is expressed as:

$$\bar{v} = Ki/n \tag{1}$$

where $\bar{v}$ is the bulk average linear groundwater velocity, K is the bulk hydraulic conductivity of the fractured rock, i is the hydraulic gradient, and n is the fracture porosity of the rock. In most types of fractured sedimentary rock in southern Ontario, n is expected to be somewhere in the range of about 0.01 to 0.00001, expressed as a fraction of the bulk rock unit volume. Thus, from Eq. 1, it is evident that even in rock with a low K value, the velocity may be large when the fracture porosity is small under conditions of moderate i values.

The main difficulty in the use of Eq. 1 for a bulk-average velocity lies in the determination of values of n. Well-accepted conventional methods can be used to determine values for K and i but there are no generally-accepted methods for determining values of n. Several methods are being investigated to determine apparent values of n so that the efficiency and accuracy of these methods can be evaluated. These methods include: pumping tests for water-table drawdown cone evaluation of n, calculation using the Snow equations based on the core description of fracture aperture and frequency, and natural and induced-gradient tracer tests.

The borehole dilution method provides a direct measure of the localized velocity rather than its indirect determination by means of Eq. 1. The test involves first isolating a test interval by means of packers and then monitoring the time-rate-of-change of a suitable tracer contained within the packed-off interval. From the concentration history measured in the packed-off interval, a simple mass balance equation allows calculation of the Darcy flux of groundwater flowing through the monitored interval. Because the shale is rich in sodium chloride, a dilute water can be used as the tracer with electrical conductance being the parameter monitored. By borehole-dilution testing at numerous depth intervals, velocity profiles so obtained can be compared to velocity profiles obtained on the bases of Eq. 1 using the independently-estimated permeability profiles obtained from the detailed hydraulic response tests as input.

An important factor not recognized by Eq. 1 is the effect of molecular diffusion of a contaminant from the fractures to the porous rock matrix. This diffusive exchange produced an "apparent" solute velocity in the fractures which is generally less than a groundwater velocity calculated on the bases of Eq. 1. Hence matrix diffusion can be regarded as an attenuation mechanism that reduces the solute flux along the primary paths of contaminant migration.

In order to investigate the potential for matrix diffusion as an attenuation mechanism in fractured shale, a natural-gradient tracer test is planned for the 1987 field season. Both a bromide and a trace amount of halogenated hydrocarbon such as trichloroethylene or dichlorobenzene will be used as tracers. It is desired to use at least two tracers with different diffusion coefficients in order to identify any differences in matrix diffusion effects that may occur. Additional multilevel devices will be installed in order to measure tracer arrival-time curves at various depths and areal locations. From these data, effective velocities can be ascertained. The depth interval having the largest connected hydraulic conductivity will be selected for tracer injection. A variety of mathematical models developed at the University of Waterloo for the problem of advective-diffusive in fractured rock can be applied to the experimental results to determine their ability to predict contaminant advance rates in such geologic settings.

Concluding Remarks

The concern regarding contaminant migration in shale relates to the possibility for contaminants from waste disposal sites or hazardous liquid spills to migrate in groundwater through the shale to locations where they can enter surface water bodies or water supply wells located in underlying aquifers. The manner in which contaminant velocities are currently predicted in shale is close to guess-work. We expect that our investigation of methods of velocity determination will provide an improved basis for consultants and government agencies to determine velocities during investigations of sites on shale.

GEOMECHANICAL INVESTIGATION OF NEAR-SURFACE FRACTURES IN CLAY TILLS

Part 2: Laboratory investigation of strength and mineralogy

Dr. M.B. Dusseault and A.G. Vorauer

Department of Earth Sciences, University of Waterloo

1.0 Introduction

The surficial overburden of Southwestern Ontario is dominated by extensive deposits of clays and clay tills which were formed within large glacial lakes or underneath thick glaciers during the Wisconsin glaciation. These fine-grained sediments are very susceptible to changes in structure and mineralogy when exposed to surface weathering, as they are in large parts of Southwestren Ontario. These physical and chemical alterations may persist to depths in excess of 10 meters depending on the type and intensity of weathering. Soderman, Kenney and Loh (1961) reported a hard to stiff crust extending to depths as great as 40 feet (12 m.) in the Lake St. Clair region of Ontario; Lo, Adams and Seychuk (1969) reported that the Nanticoke site on the north shore of Lake Erie was underlain by 20 to 35 feet (6 to 10.7 m.) of heavily dessicated and fissured clay; Quigley and Ogunbadejo (1976) presented profiles of the Sarnia clay tills which placed the depth of the weathered crust at approximately 5 meters. The physical consequences of weathering reveal themselves as changes in strength, compressibility and permeability with respect to the underlying, unweathered sediments of the same geological unit. The chemical alterations reveal themselves through leaching and precipitation of carbonates and hydroxides as well as through changes in clay mineralogy.

The objective of this particular study has been two-fold : 1) to examine, on a site-specific basis, the macrofabric of the surface clays and clay tills; 2) to determine the degree of alteration of geomechanical parameters and mineralogy along the weathered/unweathered profile of each site. In addition, a regional investigation was undertaken to obtain results that may reflect the role of different geologic and geomorphologic characteristics in producing the surface weathered zones of Southwestern Ontario.

The following three sites were chosen for the investigation: 1) the Nanticoke site located in the varved lacustrine Haldimand clays along the north shore of Lake Erie, 2) the London site located on Port Stanley till south of the City of London, 3) the Essex site located on the "water-laid" tills of the St. Clair clay plains region (Figure 1). A discussion of the geology of each site as well as the results of the first objective have been published in Part I of this study (Dusseault and Vorauer, 1985). The purpose of this paper is to report the results of the laboratory investigations undertaken during 1986, making use of large diameter Shelby tube samples collected during the field component of this study.

2.0 Results of the geomechanical testing

At each of the three sites mentionned in the preceding section, two vertical boreholes were augered using 6-inch (15.2

cm.) diameter solid stem augers. At 5-ft intervals (1.5 m.), the auger string was removed and a 4.25-inch (10.8 cm.) ID Shelby tube lowered into the hole and hydraulically driven into the soil 24 inches (61 cm.). Since the objective was to obtain samples of the weathered and unweathered zones only, the London and Essex deposits were sampled to 12 m. and the Nanticoke deposit only to 9.15 m. where bedrock was encountered. Each tube was sealed in microcrystalline wax and transported to the laboratory where the samples were extruded, sectionned and waxed for storage. Numerous fractures were visible in the upper 3 to 4.5 m. in the London and Essex deposits and down to 9.15 m. in the Nanticoke deposits. The fractures were identified by a light grey infilling material and a discolouration zone 1 to 1.5 cm thick on either side. Extensive root systems were also visible along the fracture planes especially at Nanticoke. Dark streaks, possibly manganese oxides, were common along the fracture planes of the Essex samples.

2.1 Atterberg limits and natural water contents

For each site, a depth profile showing variations in the natural water contents, plastic limits and liquid limits is presented in Figure 2. The classic profile of a weathered crust is represented in all three cases, where the natural water contents near the surface ie top 3.5 to 4.0 m., are below the plastic limits of the soils. A feature which is common to the London and Essex tills is that the water contents are very close to the plastic limits (18-21). This is an initial indication of the behaviour of the soils which possess the characteristics of both semi-solids and plastic solids. Their generalized stress-strain curves would show a quick mobilization of the peak strength at small strains followed by a gradual loss in strength at larger strains. The liquid limits range between 32 and 36 and in both cases do not vary significantly with depth. The Nanticoke lacustrine clays are more plastic than the tills and exhibit higher plastic and liquid limits. The anomalously low Atterberg limits at 6 m. are believed to be testing errors and not indicative of inherent variations within the varved deposits.

The Casagrande plasticity chart shown in Figure 2 represents clearly the plasticity groupings aforementionned. The data points plotting above the A-line indicate that the fines fraction of all three soils is dominated by inorganic clays. A simple identification of the dominant clay minereal in the soils can be made using the plasticity chart published in Holtz and Kovacs (1981, p.89). The Atterberg limit data plotting just above the A-line is representative of illitic clays.

It most be stated that the water content profiles of Figure 2 are not, on their own, indicative of the ultimate depth of desiccation but rather represent a minimum depth.

2.2 Oedometer consolidation tests

The purpose of this series of tests was to determine the overconsolidation ratio (OCR) associated with the weathered/unweathered profiles at all three sites. The results of the testing are shown in Figure 3 as plots of void ratio versus logarithm of effective stress. One of the obvious characteristics of all of the curves shown is the absence of any distinctive break in their slope as is generally expected once the preconsolidation pressure has been exceeded. The gentle curvature of the e-log effective stress plots has been associated with weathered clays in the upper crust by Bjerrum (1973). These plots are representative of a reduced compressibility compared with that of the unweatherd clay, due to formation of aluminium and iron hydroxides acting as weak cement. Sample disturbance is another factor which may affect the void ratio-effective stress behaviour as shown by Schmertmann (1955). Schmertmann developed a procedure for testing overconsolidated clays taking into account sample disturbance. His procedure includes a cycle of partial unloading and reloading starting at the approximate preconsolidation pressure. This procedure has also been recommended by Leonards (1976) to attempt to reproduce as closely as possible the in-situ stress state ie geological unloading from the maximum overburden pressure.

Table 1 shows the results obtained from the Schmertmann procedure:

	Depth (m.)	OCR	Cc	Cr
London #3	4.57	4.08	0.178	0.019
London #12	6.10	3.45	0.165	0.028
London #13	7.62	1.55	0.182	0.027
London #15	10.70	2.19	0.222	0.024
Essex #1	1.37	8.52	0.142	0.032
Essex #2	3.05	3.35	0.140	0.030
Essex #3	4.57	5.62	0.244	0.030
Essex #4	6.09	5.00	0.251	0.024
Essex #6	9.15	1.90	0.215	0.028
Nanticoke #1	1.52	8.10	0.220	0.040
Nanticoke #2	3.05	5.90	0.315	0.043
Nanticoke #3	4.57	3.10	0.332	0.053
Nanticoke #4	6.10	2.10	0.343	0.048
Nanticoke #5	7.62	1.09	0.405	0.043

OCR = preconsolidation pressure/existing overburden pressure
Cc = compression index
Cr = recompression index

There are several mechanisms which have acted upon the clays and clay tills of Southwestern Ontario to produce the overconsolidation observed in the oedometer tests. The London site has been subjected to a change in total stress produced by deglaciation followed by chemical alteration and desiccation due to surface drying. The near surface samples proved to be so brittle that placement of the consolidation ring lead to large disturbances of the samples. The increase in OCR at 10 m. may reflect a sample obtained from the underlying Westminster Moraine which was overidden during the deposition of the Port Stanley till. The Essex site located in the "water-laid" tills near Lake St. Clair was probably subjected to a change in pore pressure due to groundwater lowering which accompanied a general lowering of lake levels between 12,000 and 8,000 years B.P. (Soderman and Kim, 1970). This was then followed by desiccation and chemical weathering at the near surface producing large apparent OCR's. The Nanticoke site has also been subjected to changes in pore pressure due to groundwater lowering but not to the same degree as the Essex site, as evidenced by comparatively lower OCR's. The higher void ratios at the Nanticoke site (Figure 3) are due to the lacustrine origin of this deposit.

The compression indices from all three sites show a generally increasing trend with depth indicating that there has been lesser structural alteration. The recompression indices appear to be independent of depth and OCR and they are not parallel to the final rebound curves.

2.3 Laboratory hydraulic fracture tests

An investigation into the tensile strength of the weathered and unweathered clays was undertaken as this parameter may have a controlling influence upon the behaviour of the fractured and non-fractured material subjected to tensile stresses. These stresses can develop at the bottom of large excavations such as those constructed for the disposal of liquid and solid wastes. Soil rupture or fracture reopening could prove detrimental to the integrity of such waste disposal facilities.

A laboratory hydraulic fracture test was developed by Decker and Clemence (1981) to study the hydraulic fracture initiation in compacted soils. They determined that a series of hydraulic fracture tests could be used to calculate an acceptable value for the tensile strength of the soil. The test involved inserting a small diameter needle with radial outlet ports into the middle of a compacted soil of low plasticity. The soil would then be consolidated under an appropriate effective cell pressure until complete consolidation was attained. Fracturing of the sample would then be accomplished by uniformly increasing the fluid pressure within the injection needle, until an abrupt increase in flowrate occurred indicating failure of the sample. A series of three to four of this tests would be completed using different samples consolidated under higher confining pressures. The analysis then involved plotting the data on a confining pressure versus failure pressure plot and drawing a straight line through the points. The failure pressure at zero confining pressure was taken as the tensile strength of the soil. A variation on this type of laboratory method was also attempted by Bjerrum and Andersen (1972) in studying the measurement of lateral earth pressures. They stated that the critical water pressure at which permeability increased abruptly was related to the effective stresses around a piezometer tip as well as the tensile strength of the soil.

In the present study, 4-inch (10 cm.) diameter and 8-inch (20 cm.) long samples of undisturbed clay were tested. Fluorescein dye was added to the injection fluid as recommended by Bjerrum and Andersen (1972) since they observed that without a tracer, the induced fracture would not have been visible upon sectionning of the sample. This may have been due to the reconsolidation of the clay following pressure relief.

The results of the hydraulic fracture tests are presented in Figure 4 as a plot of confining pressure versus rupture pressure, along with the data presented by Decker and Clemence (1981) for compacted low plasticity soil. In general, the results for the undisturbed clays plot at much higher rupture pressures than for the compacted soils. Samples tested more than once show a trend of rupture pressures less than those tested only once at any given confining pressure. This may be due to a remoulding of the soil along the induced flow path within the sample. Some of the intact and fractured samples do plot along a linear trend who's regression provides an abscissa intercept at 51 kPa (r = 0.894). However, the significance of this tensile strength value remains unclear as both weathered and unweathered, and intact and fractured samples were tested. Following the early tests on intact clays, no fluorescein could be detected under ultra-violet light. The concentration of the tracer was subsequently increased for the tests on fractured samples, which then allowed visual confirmation of induced flow paths along fracture planes adjacent to the probe outlets.

Ingles (1962) has stated that high capillary stresses will develop in a partially saturated soil due to the formation of capillary menisci between particles. The results of his analysis lead to an empirical equation that relates tensile strength in kPa to a/d where a is in the range of 250 to 650 and d is the particle diameter in mm.. In fact, capillary stresses would be more directly related to the pore sizes in the soil which indicates that tensile strength may be dependent on soil structure, and in the case of clays also related to the effective confining pressures. It seems reasonable to suggest than, that at lower void ratios a partially saturated soil may exhibit greater tensile strength. This may help to explain the apparent increase in the tensile strength component of the rupture pressure with increasing confining pressure.

2.4 Consolidated-undrained triaxial tests

The objective of this series of tests was to examine any differences in stress-strain behaviour and strength between the weathered and unweathered zones at all three sites. To maintain sample homogeneity and to eliminate the time needed for sample preparation, the multi-stage triaxial testing method was used (Bishop and Henkel, 1972). This method requires only one sample to adequately define the shear strength envelope. It involves consolidating a sample at a particular effective cell pressure followed by slow shearing until just before failure. The same sample is then unloaded and reconsolidated at a higher effective cell pressure which is then followed by shearing again. Three tests at different effective cell pressures are usually required to determine the shear strength parameters.

The 10 cm. diameter by 20 cm. long samples were used for the triaxial testing to reduce the effect of sample size on shear strength. All samples were consolidated isotropically before shearing and a minimum saturation back-pressure of 207 kPa was used to dissolve any air in the sample and in the water lines (Bishop and Henkel, 1972). Skempton's B-parameter (change in pore pressure/change in cell pressure) was determined before each test and ranged between 0.85 and 0.96. For stiff soils, these B-values correspond to saturations greater than 96% (Black and Lee, 1973).

For the multi-stage tests, it was assumed that failure had occurred at maximum deviator stress. The strain-rate for all tests was 0.0012 inches/min. or 0.9%/hr.

The results from all CIU triaxial tests are presented in Figures 5 to 10 in terms of plots of shear stress versus strain, change in pore pressure versus strain and Q versus P. In all six cases, the soils show an overconsolidated behaviour which is exemplified by a decreasing pore pressure as peak shear strength is approached. This is associated with the phenomenon of dilation which is commonly observed in dense sands and overconsolidated clays. The fact that the change in pore pressure does not become negative indicates that these deposits are not heavily overconsolidated such as the England clays. The stress path plots (Q vs. P) are also indicative of overconsolidated soils and the maximum confining pressures of 207 and 240 kPa do not seem to have brought the soils into their normally consolidated state.

The secant moduli, taken at 50% of peak strength, is a function of confining pressure and sample depth, with higher elastic moduli being associated with the surface weathered crust. In general, the magnitude of the moduli are related in the following manner: Essex > London > Nanticoke. Since the elastic modulus is very sensitive to sample disturbance it is not surprising that the London moduli are smaller than the Essex moduli since they were much more difficult to sample using the Shelby tubes. This may be supported by the fact that the peak shear strengths of the London samples are higher than those from Essex. The following table summarizes the shear strength parameters developed from the stress path plots:

Table II

	C '(kPa)	PHI '
Nanticoke #1-1	13	36
Nanticoke #1-5	50	15
London #1	38	31
London #16	12	34
Essex #2	47	31
Essex #13	41	23

The Nanticoke surface sample shows the results of shear behaviour dominated by the movement of soil blocks along fissure planes. The confining pressures were not high enough to begin mobilizing the cohesion of the clay matrix material such as in the deeper sample showing high cohesion and low angle of friction. This phenomenon has also been reported by Baracos et al (1980) in their study of the Winnipeg lacustrine clays. The high cohesion and angle of friction values associated with the London and Essex samples is a reflection of their overconsolidated nature and till structure.

3.0 Clay mineralogy

The objective of the mineralogical analysis was to examine the results of weathering on the bulk clay mineralogy and also any differences in mineralogy between the weathered clay matrix and the coatings along the fracture plains. The X-ray diffraction technique was used for this purposes along with three samples from each of the study sites: one from the near-surface, another containing obvious infilled fracture planes and another from the unweathered zone at depth. Each sample was pre-treated for excess carbonate removal by mixing with a solution of sodium acetate and acetic acid. The less than 2 micron fraction was obtained using a standard sedimentation process and a small portion of the soil/water mixture was aloud to settle onto circular glass lenses. The following five treatments were performed preceding X-ray diffraction analysis at the University of Guelph facilities: 1) Mg - saturated, 2) Mg - saturated, glycol solvated, 3) K - saturated, air-dry, 4) K - saturated, heated to 500 C for 1 hr., 5) boiling in concentrated HCl for 15 minutes.

The following is a descriptive analysis of the results obtained. All of the samples showed basically the same trends, the clay minerals being dominated by the presence of illite with minor amounts of Fe-chlorite. Small amounts of vermiculite were also present in most samples, identified by a reduction of the 14 A peak and an intensification of the 10 A peak upon K saturation (Soderman and Quigley, 1965). Traces of kaolinite were also present in the Essex and Nanticoke clays evidenced by 7 A peak remaining after the HCl treatment. Interstratified minerals such as illite-chlorite were present in the London samples, as a persistant 8.4 A peak throughout the treatment process (Soderman and Quigley, 1965). No obvious amounts of smectite were detected in any of the samples although a decrease in Fe-chlorite peaks was noted in the near-surface samples from Essex and London. Quigley and Ogunbadejo (1973) noted this phenomenon in the Sarnia clay tills and correlated it with iron oxidation leading to swelling clay formation. Any swelling minerals in the samples tested for this study may only be present as interstratified clays such as illite-smectite or vermiculite-smectite evidenced by high backgrounds and short peaks in the low angle range ie greater than 24 degrees, (Mitchell, 1976). The fact that the samples were allowed to air-dry onto the glass lenses may have collapsed the smectite minerals permanently, not allowing re-swelling upon glycolation.

4.0 Conclusions

This study has examined the consolidation, strength and mineralogical characteristics of the weathered/unweathered profiles at three geologically different sites across Southwestern Ontario. The clays at all three sites have proven to be overconsolidated down to depths of at least 12 m. with the till deposits showing the largest degree of overconsolidation. Shear strength anisotropy does exist between the weathered and unweathered clays with the greatest difference occuring at the Nanticoke site. A laboratory tensile strength method has been attempted with the clay samples, however results are largely inconclusive at this point because direct testing of fractures within the samples proved difficult. This strength parameter should be given more attention especially in terms of constructing deep excavations for waste disposal. Silvestri and Tabib (1983) used a theoretical procedure to determine gravity stresses in finite elastic slopes. From their contoured diagrams of normalized stresses, it is evident that significant tensile stresses can develop at the base of excavations with the deepest zone of negative horizontal stress being associated with high angle, non-vertical slopes. For example, a 10 m. deep excavation with 60 degree slope in a material with unit weight of 20 kN/m3 and Ko=0.5 will have a tensile stress of 100 kPa generated at the base. Large amounts of swelling clays have not been detected in the near-surface matrix and fracture samples examined in this study. Vermiculite, which has a certain swelling potential, has been identified in small amounts in several near-surface samples. More detailed study of the mineralogy and potential tensile strength of the near-surface clays in Southwestern Ontario is required before an adequate understanding of the behaviour of fractured clays can be attained on a regional basis. The constant need to develop waste management facilities in less geologically favourable environments, underlain by thinner fine-grained units, will require a clearer understanding of this most difficult construction material.

Acknowledgements

This research has been funded by an Ontario Ministry of the Environment research grant RAC 147 PL. We also wish to thank Mr. B. Pett, supervisor at the Nanticoke Water Pumping Station, Mr.

J. Mullins, supervisor of Essex County Landfill #3 and Mr. Choma, environmental engineer for the City of London, for the helpful cooperation in allowing site access and providing site investigation reports. We also wish to thank Jim Wong and Sam Vales for their assistance during the collection of the samples.

References

Baracos, A., J. Graham and L. Domascuk. 1980. Yielding and rupture in a lacustrine clay. Can. Geot. Jr., Vol 17, pp. 465-645.

Bishop, A.W. and D.J. Henkel. 1972. The measurement of soil properties in the triaxial test. Edward Arnold Publishers Ltd., 2nd Edition, London, 227 p.

Bjerrum, L.. 1973. Problems of soil mechanics and construction on soft clays and structurally unstable soils. General Report, Session 4, Proc. 8th Int.Conf. S.M.F.E., Vol. 3, pp.111-159.

Bjerrum, L. and K.H. Andersen. 1972. In-situ measurement of lateral pressures in clay. Proc. 5th European Conf. S.M.F.E., Madrid, Vol. 1, pp. 29-38.

Black, D.K. and K.L. Lee. 1973. Saturating laboratory samples by back pressure. Jr. Soil Mech. Fnd. Eng., ASCE, Vol. 99, SM1, pp. 75-93.

Decker, R.A. and S.P. Clemence. 1981. Laboratory study of hydraulic fracturing in clay. Proc. 10th Int. Conf. S.M.F.E., Stockholm, Vol. 1, pp.573-575.

Dusseault, M.B. and A.G. Vorauer. 1985. Geomechanical investigation of near-surface fractures in clay tills, Part I: Fracture mapping at three sites in Southwestern Ontario. Proc. Tech. Transfer Conf. No. 6, Toronto, Part 3, pp. 266-291.

Holtz,R.D. and W.D. Kovacs.1981. An introduction to geotechnical engineering. Prentice-Hall Inc., New Jersey, U.S., 733 p.

Ingles,O.G..1962. Bonding forces in soils, Part 3: A theory of tensile strength for stabilised and naturally coherent soils. Proc. 1st Conf. Australian Road Research Board, Vol. 1, pp. 1025-1047.

Leonards,G.A. 1976. Estimating consolidation settlements of shallow foundation on overconsolidated clays. Special Report 163, Transportation Research Board, pp. 13-16.

Lo,K.Y., J.I. Adams and J.L. Seychuk. 1969. The shear behaviour of a stiff fissured clay. Proc. 7th Int Conf. S.M.F.E., Mexico, Vol. 1, pp. 249-255.

Mitchell,J.K.. 1976. Fundamentals of soil behaviour. J. Wiley and Sons, Inc., New York, 422 p.

Quigley,R.M. and T.A. Ogunbadejo. 1976. Till geology, mineralogy and geotechnical behaviour, Sarnia, Ontario. Proc. Conf. Glacial Tills, Special Publ. 12, R. Soc. Can., R.F. Legget (Ed.), pp.336-345.

Schmertmann,J.H.. 1955. The undisturbed consolidation behaviour of clay. Transactions, ASCE, Vol.120, pp. 1201-1233.

Silvestri,V. and C. Tabib. 1983. Exact determination of gravity stresses in finite elastic slopes: Part II. Applications. Can Geot. Jr.,Vol.20, no. 1, pp. 55-60.

Soderman,L.G., T.C. Kenney and A.K. Loh. 1961. Geotechnical properties of glacial clays in Lake St.Clair region of Ontario. Proc. 14th Canadian Soil Mech. Conf., Nat. Res. Council Tech. Mem. 69, pp. 55-81.

Soderman,L.G. and Y.D. Kim. 1970. Effect of groundwater levels on stress history of St. Clair till deposits. Can. Geot. Jr., Vol. 7,pp. 173-187.

Soderman,L.G. and R.M. Quigley. 1965. Geotechnical properties of three Ontario clays. Can. Geot. Jr., Vol. 11, no. 2., pp.167-189.

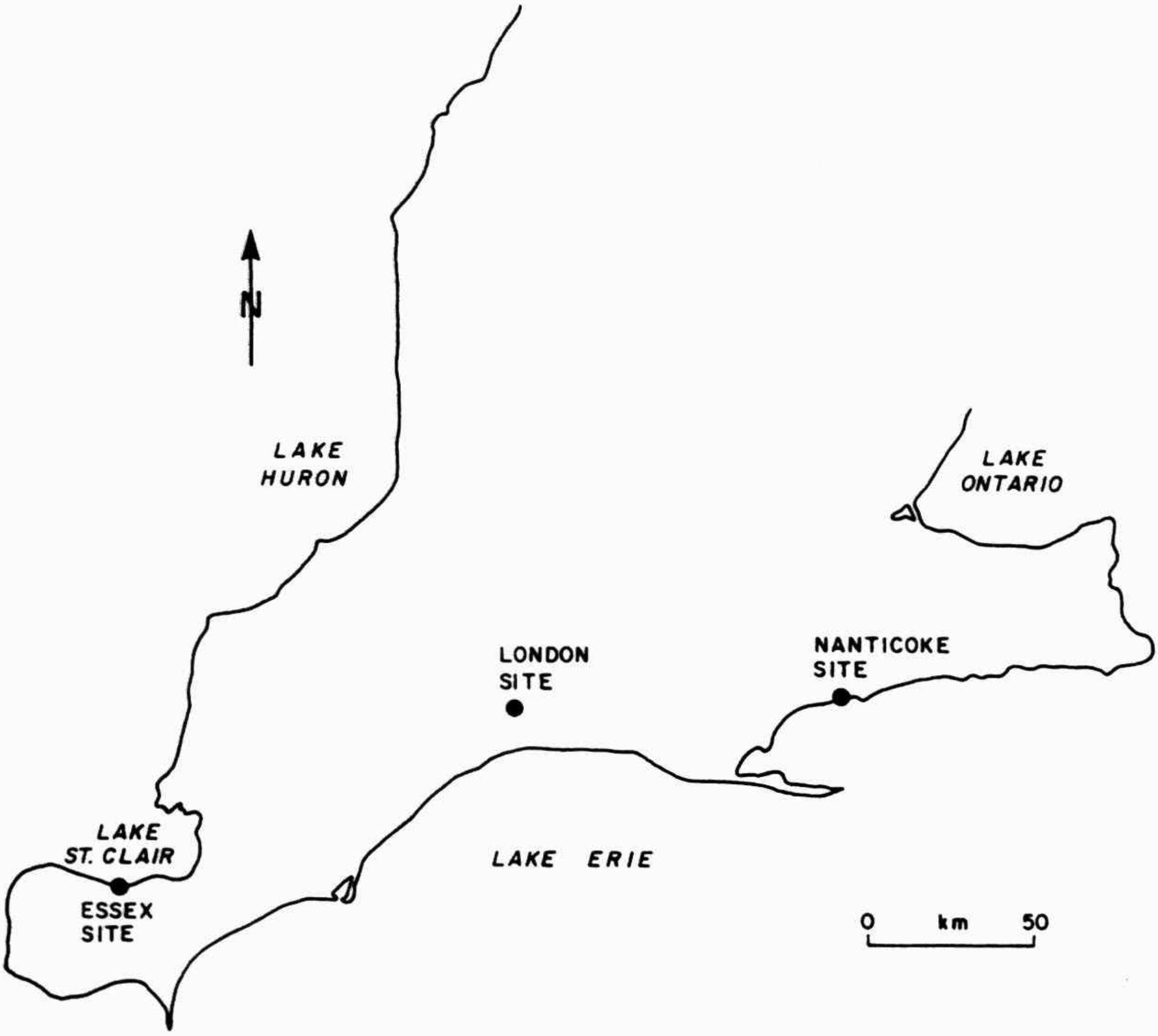

N
LAKE HURON
LAKE ONTARIO
LONDON SITE
NANTICOKE SITE
LAKE ST. CLAIR
ESSEX SITE
LAKE ERIE
0 km 50

Figure #1

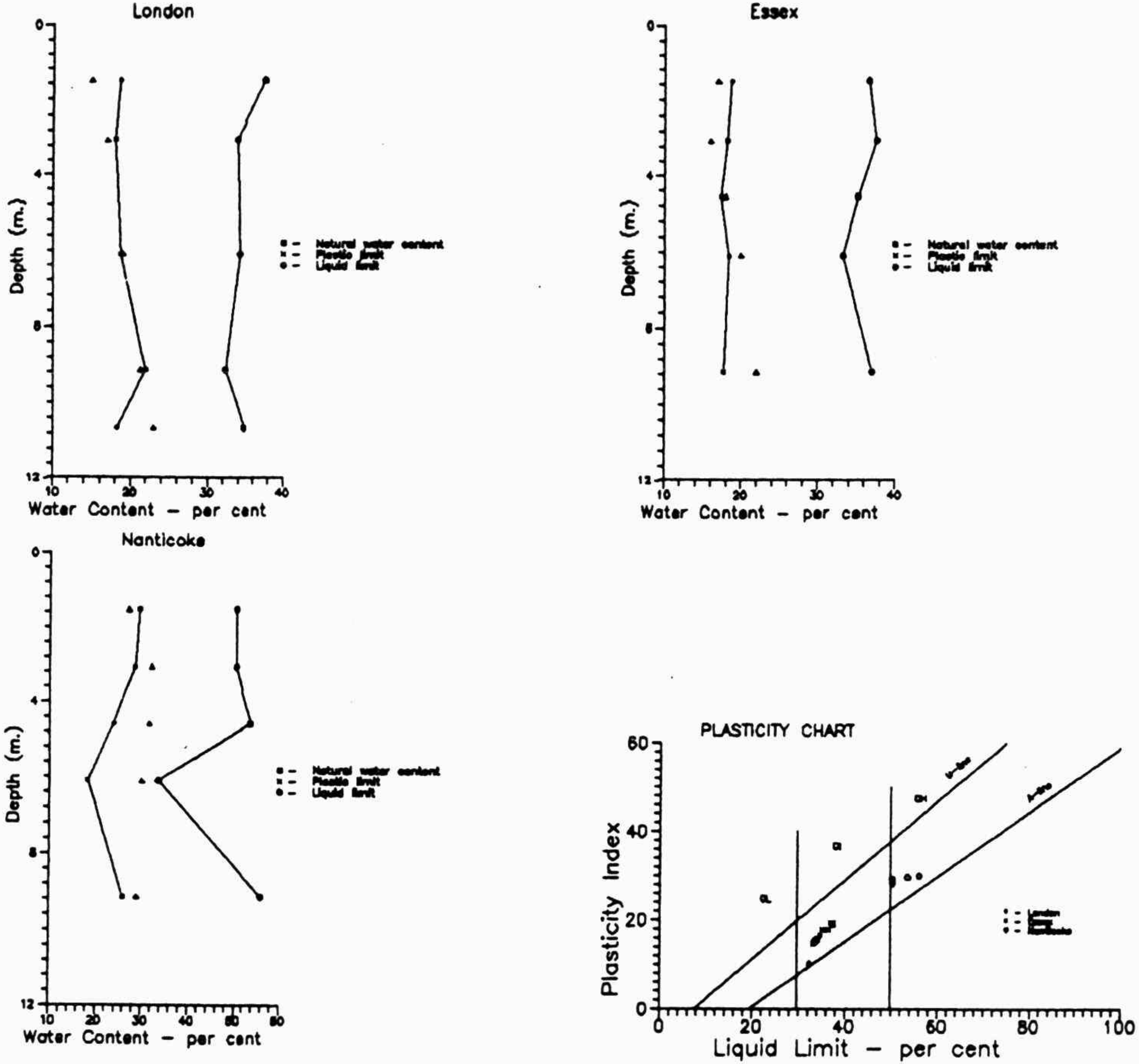

London
Essex
Nanticoke
PLASTICITY CHART
Depth (m.)
0
4
8
12
Water Content – per cent
10
20
30
40
50
60
● – Natural water content
▲ – Plastic limit
● – Liquid limit
Plasticity Index
Liquid Limit – per cent
0
20
40
60
80
100
CL
CI
CH
U-line
A-line
London
Essex
Nanticoke

Figure #2

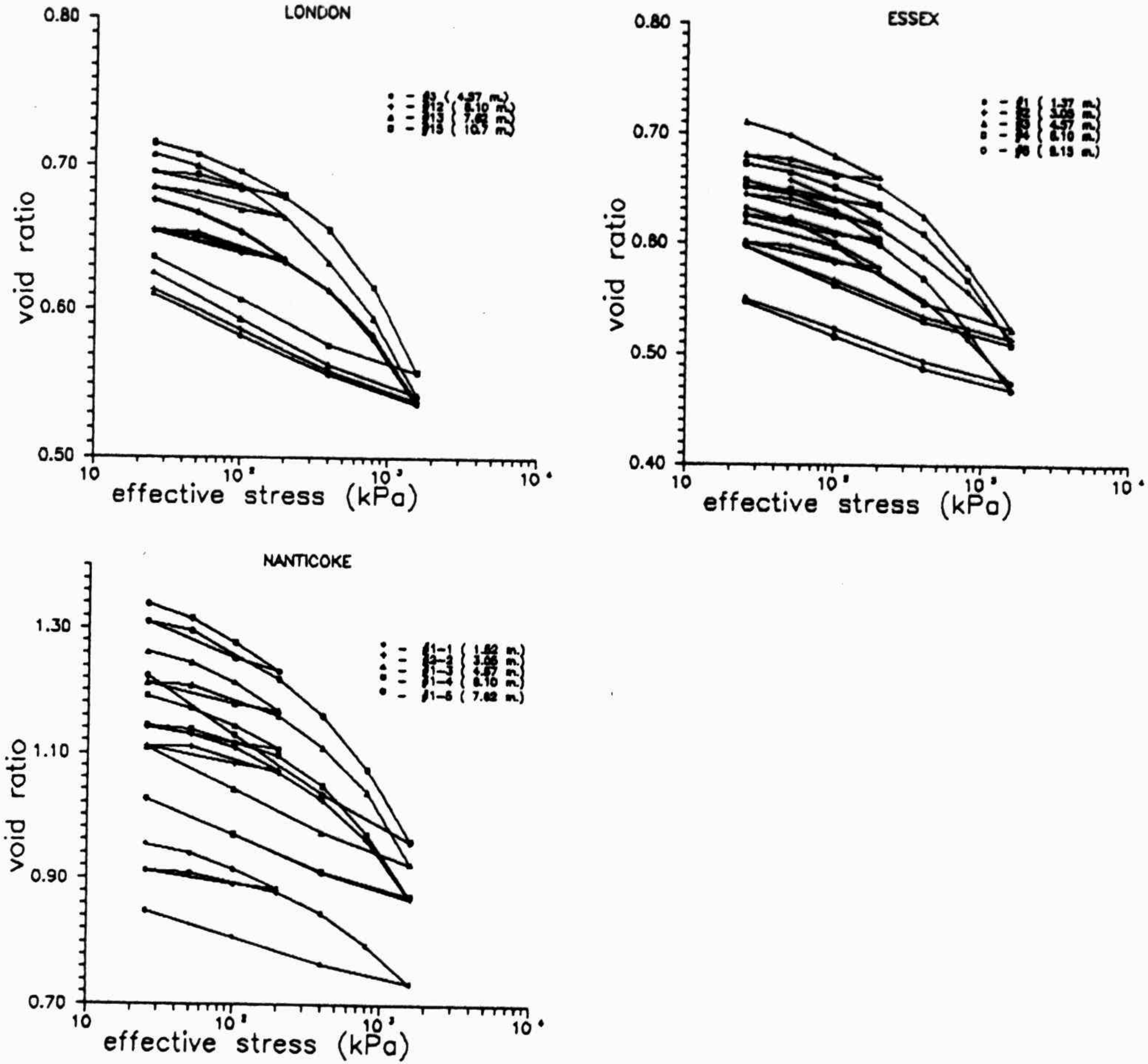

LONDON
void ratio
0.80
0.70
0.60
0.50
10
10²
10³
10⁴
effective stress (kPa)
● – #3 (4.57 m.)
◆ – #12 (6.10 m.)
▲ – #13 (7.62 m.)
■ – #15 (10.7 m.)
ESSEX
void ratio
0.80
0.70
0.60
0.50
0.40
10
10²
10³
10⁴
effective stress (kPa)
● – #1 (1.37 m.)
◆ – #2 (3.05 m.)
▲ – #3 (4.57 m.)
■ – #4 (6.10 m.)
○ – #5 (9.15 m.)
NANTICOKE
void ratio
1.30
1.10
0.90
0.70
10
10²
10³
10⁴
effective stress (kPa)
● – #1-1 (1.52 m.)
◆ – #1-2 (3.05 m.)
▲ – #1-3 (4.57 m.)
■ – #1-4 (6.10 m.)
● – #1-5 (7.62 m.)

Figure #3

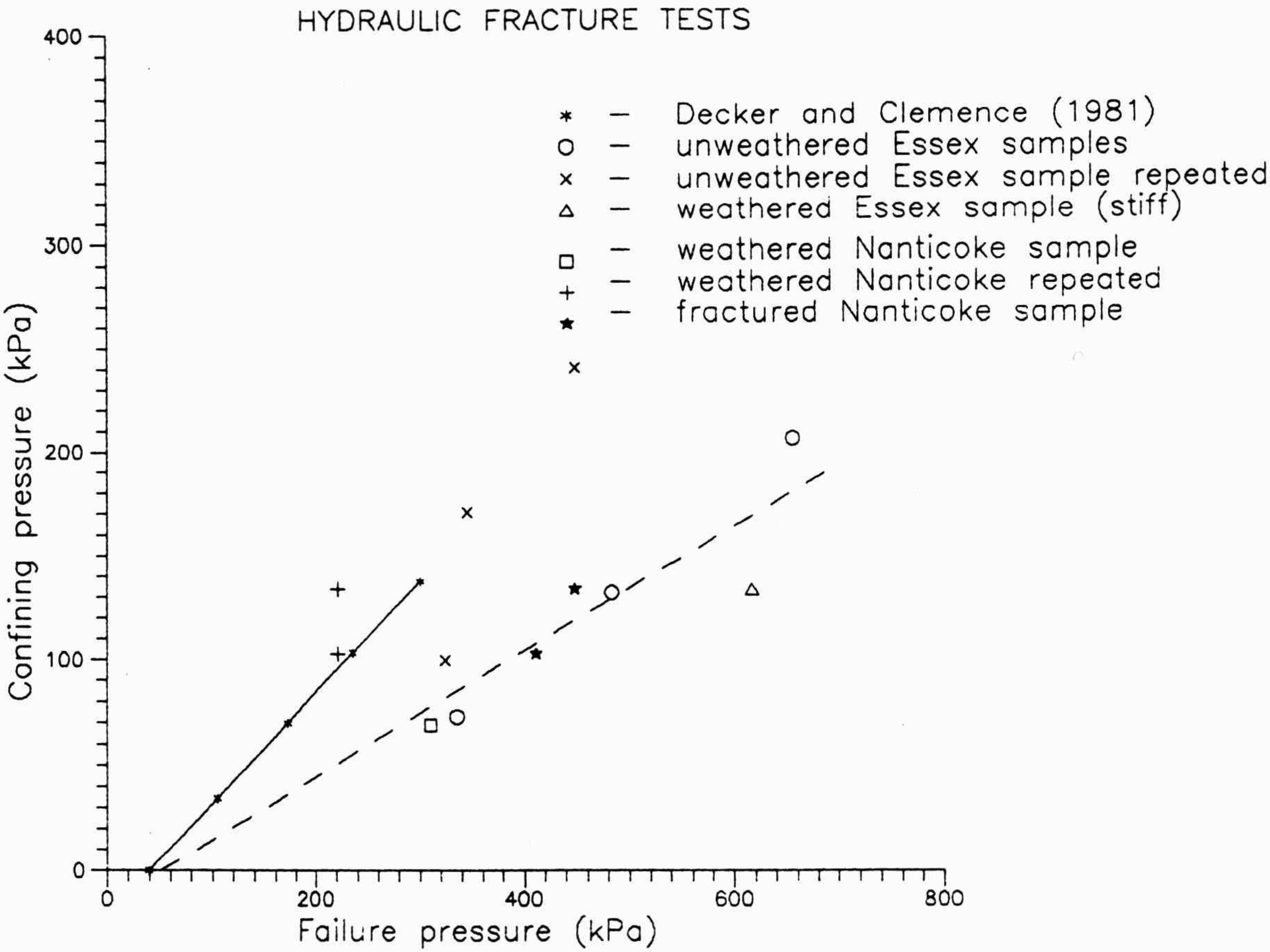
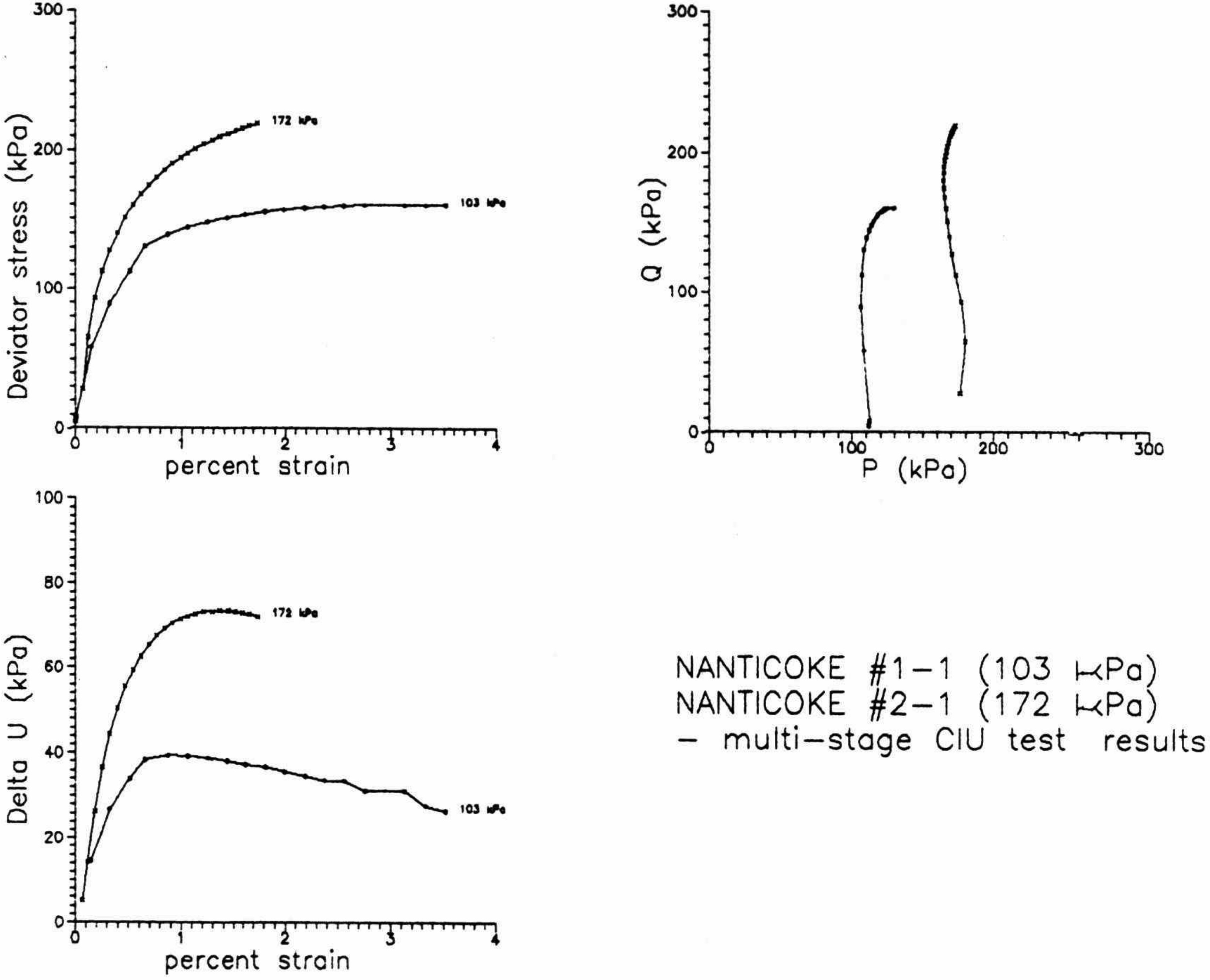

HYDRAULIC FRACTURE TESTS
* — Decker and Clemence (1981)
○ — unweathered Essex samples
× — unweathered Essex sample repeated
△ — weathered Essex sample (stiff)
□ — weathered Nanticoke sample
+ — weathered Nanticoke repeated
★ — fractured Nanticoke sample
Confining pressure (kPa)
0
100
200
300
400
Failure pressure (kPa)
0
200
400
600
800

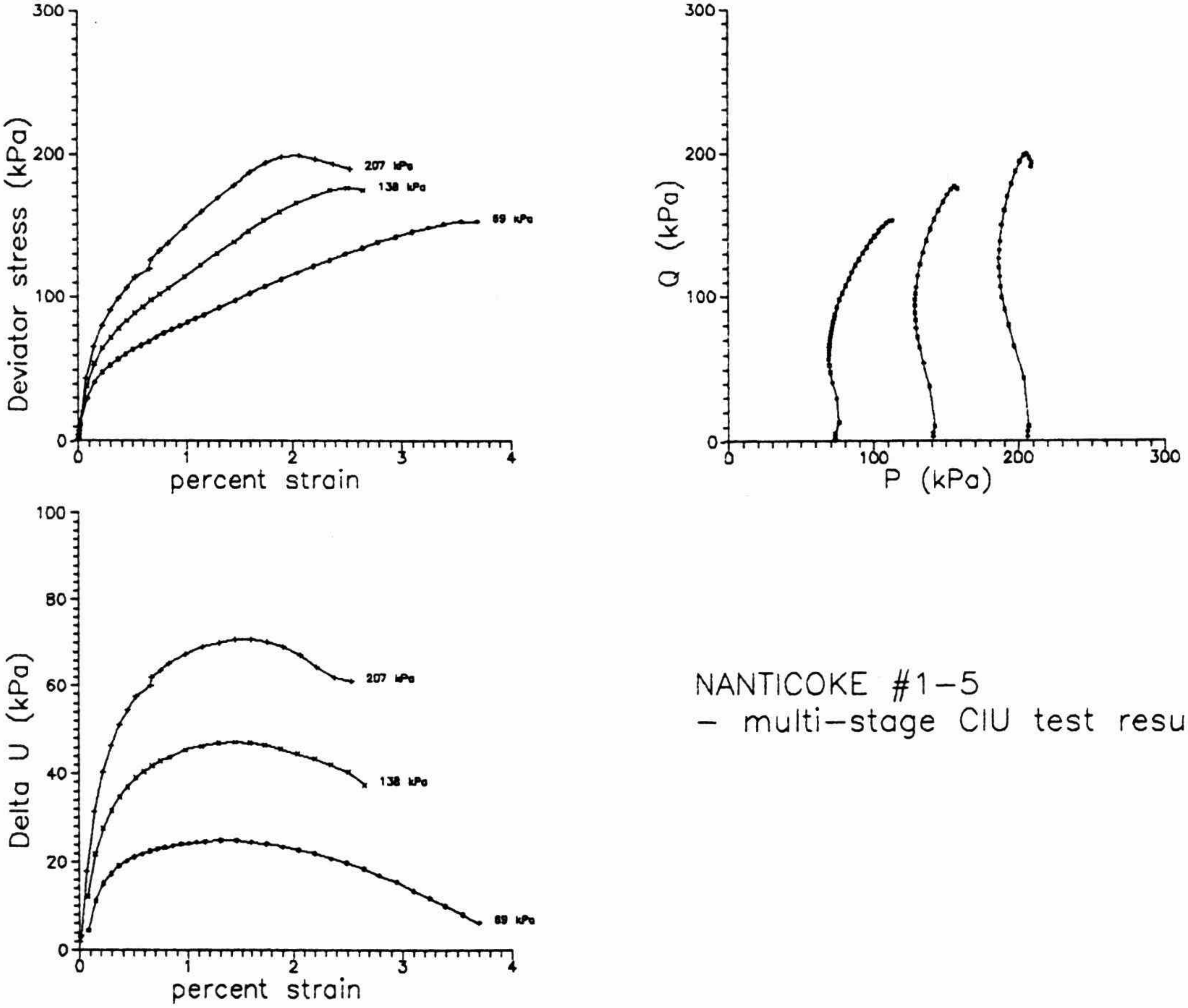
Figure #4



NANTICOKE #1-1 (103 kPa)
NANTICOKE #2-1 (172 kPa)
- multi-stage CIU test results

Figure #5

Figure #6



NANTICOKE #1-5
- multi-stage CIU test results

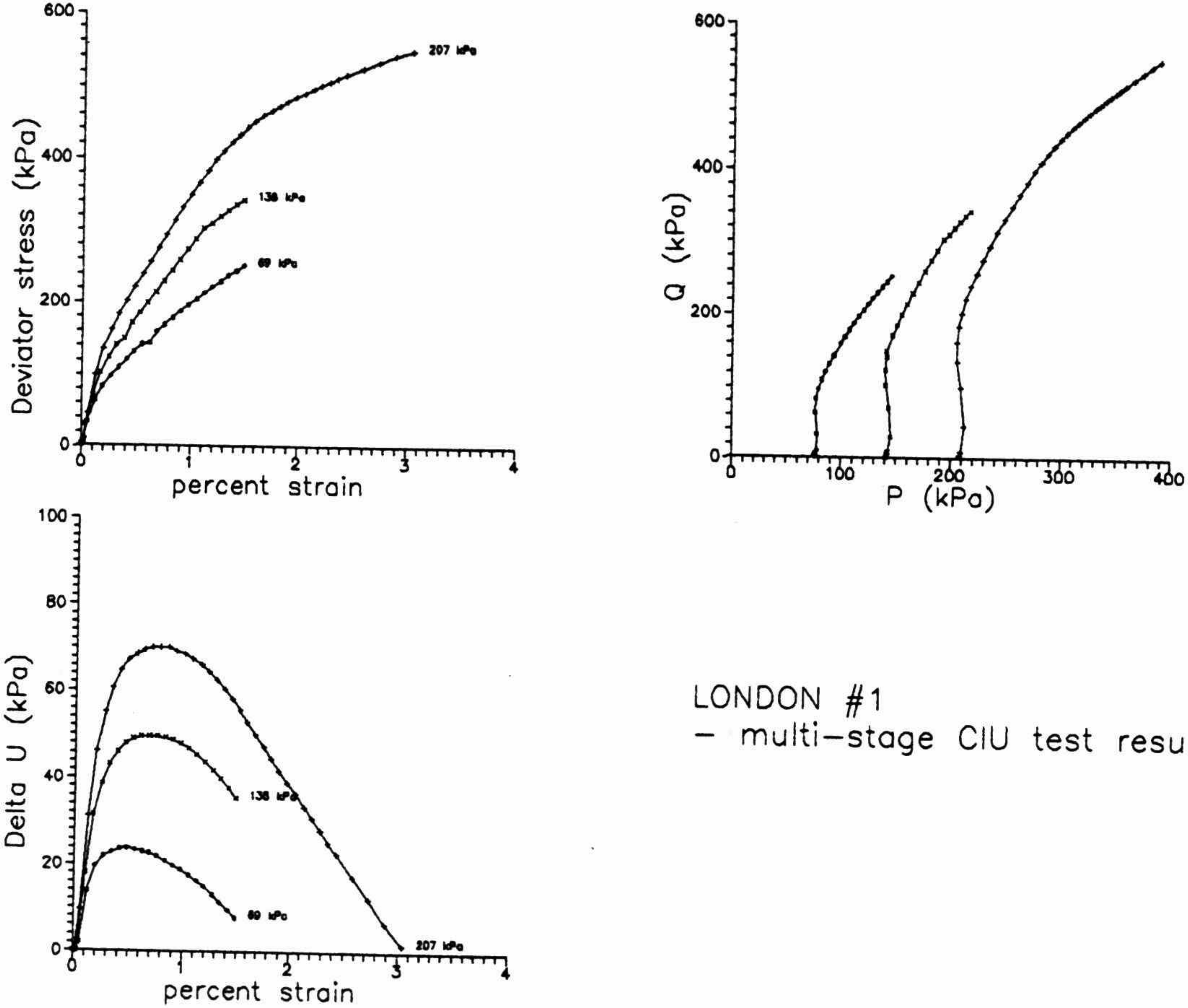
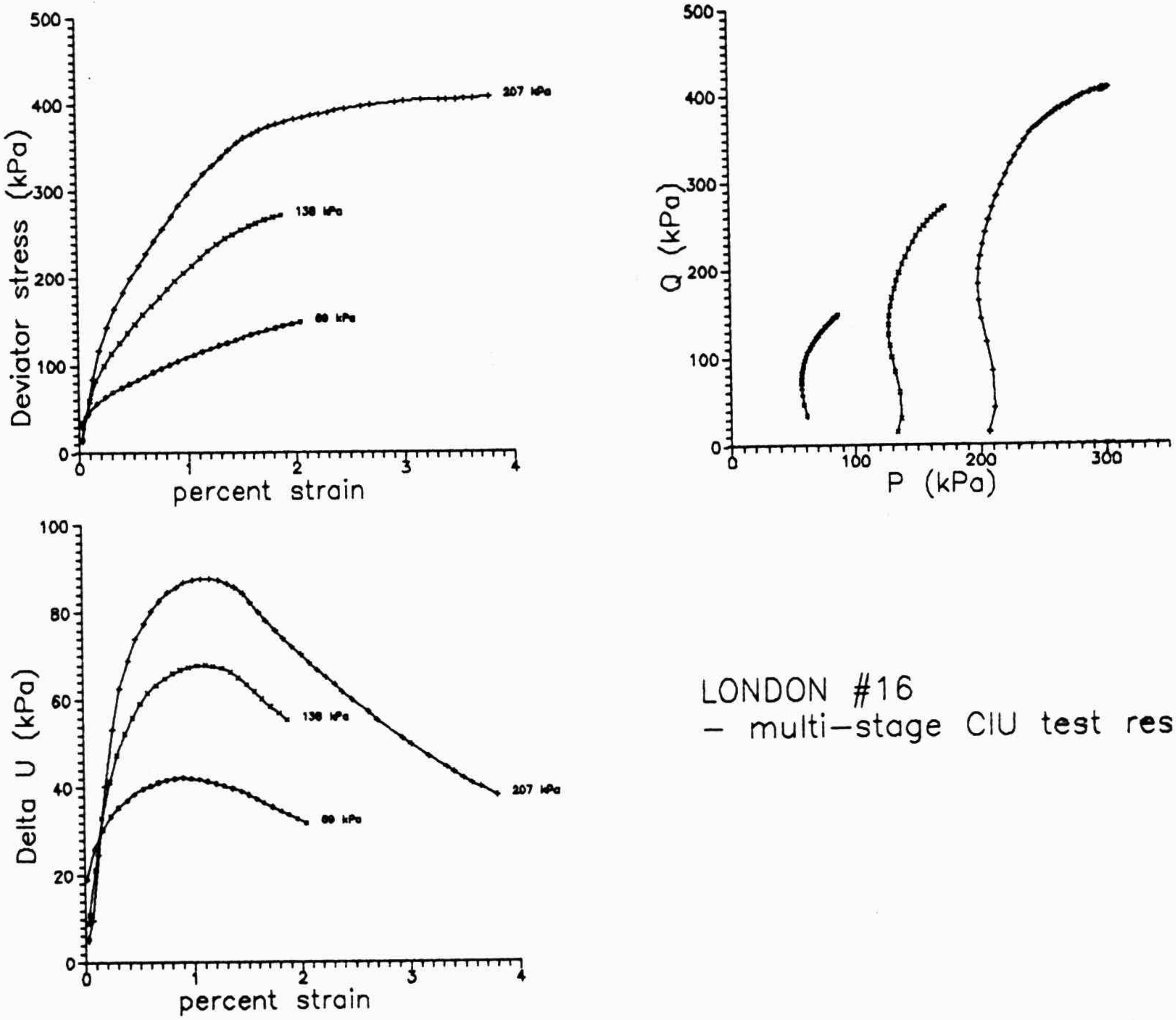


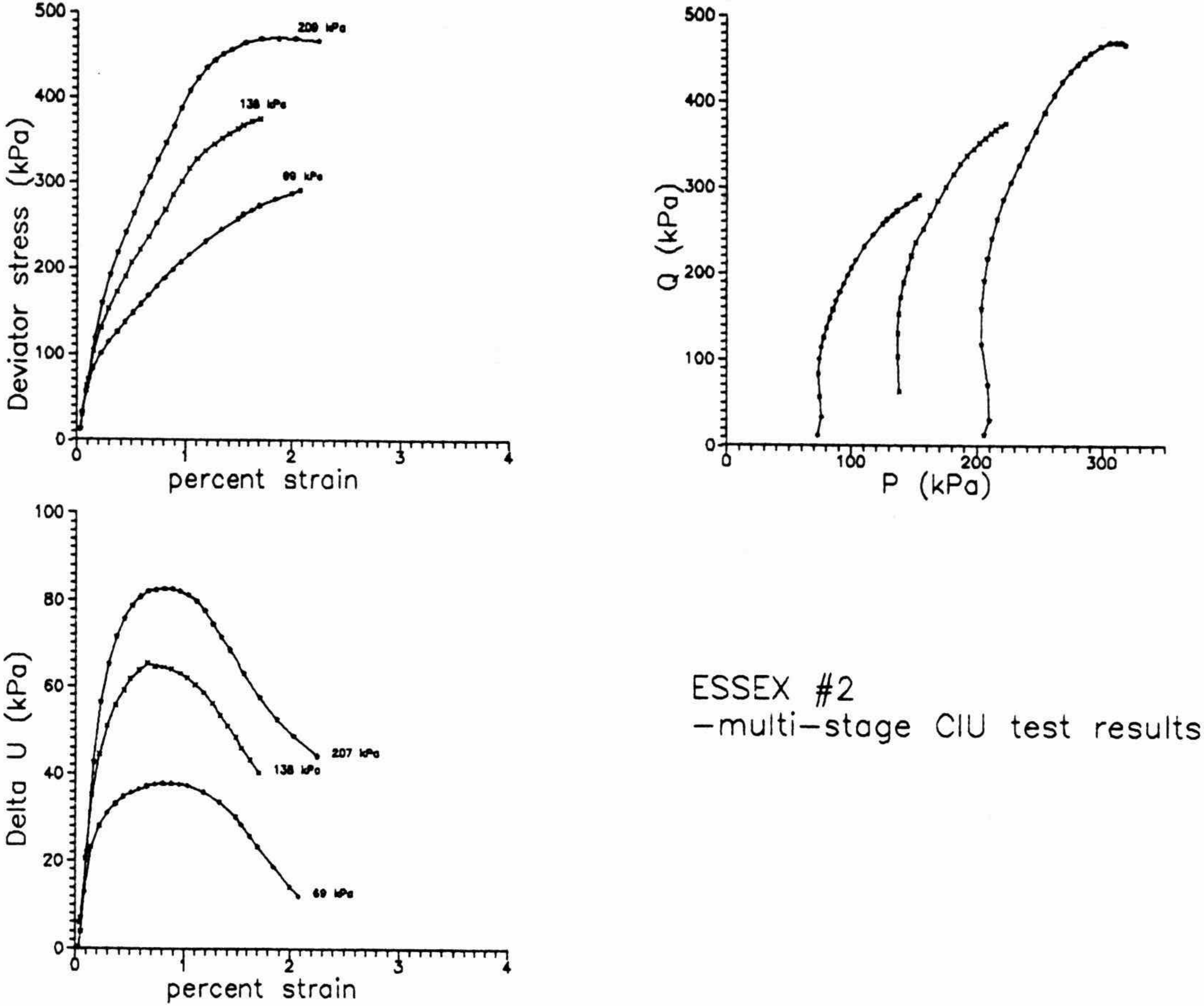
Figure #7

LONDON #1
- multi-stage CIU test results

Figure #8

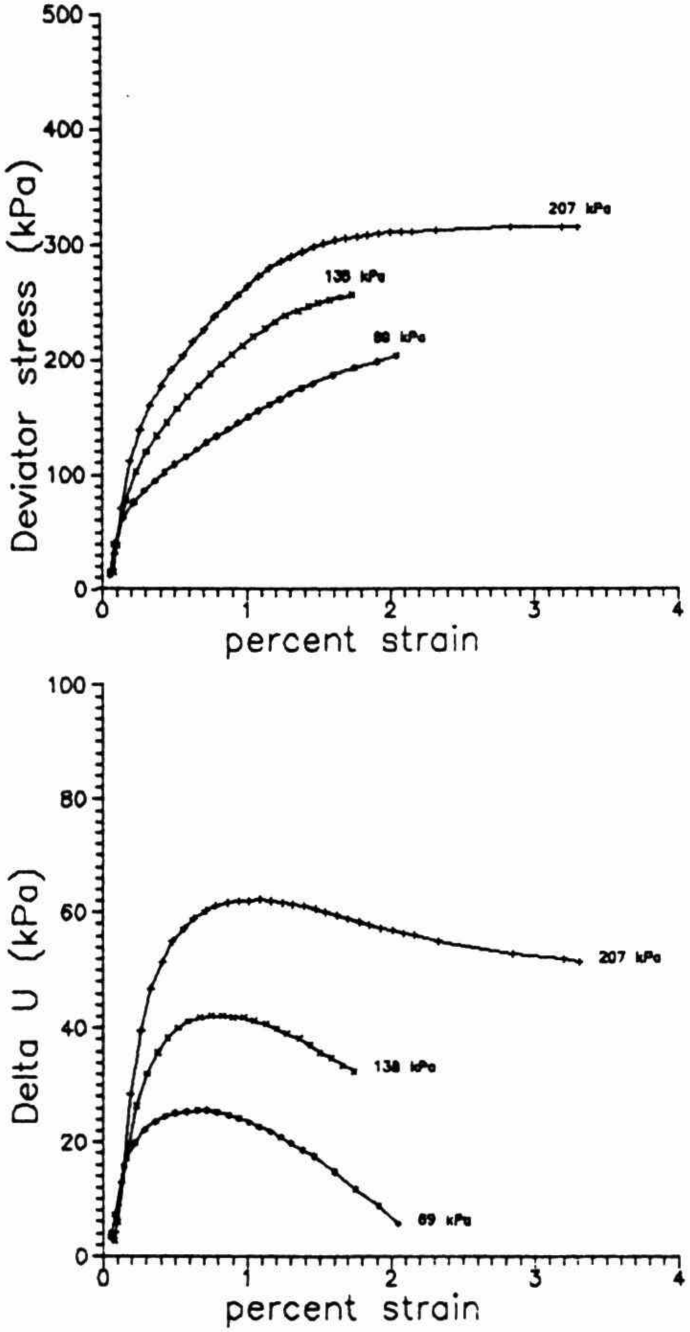


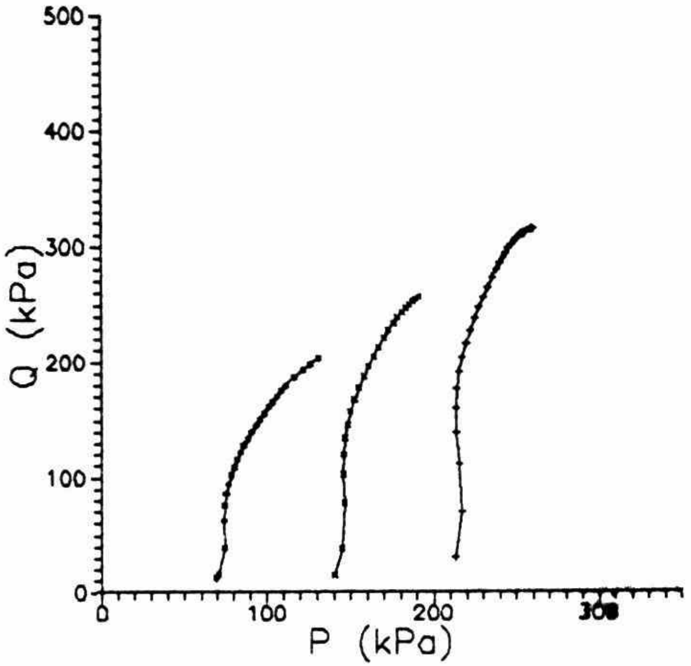
LONDON #16
– multi–stage CIU test results



ESSEX #2
-multi-stage CIU test results

Figure #8





ESSEX #13
- multi-stage CIU tests results

Figure #10

ORIGINS OF ELEVATED CHLORIDE CONCENTRATIONS IN GROUNDWATER SYSTEMS

P.E. PILON and K.W.F. HOWARD

GROUNDWATER RESEARCH GROUP
UNIVERSITY OF TORONTO, SCARBOROUGH CAMPUS,
SCARBOROUGH, ONTARIO M1C 1A4

Key words: Groundwater, Chloride Enrichment, Hydrochemistry

ABSTRACT

Shallow aquifer systems in southern Ontario frequently exhibit elevated chloride concentrations that locally exceed water quality guidelines. While in some cases the elevated chloride concentrations can be attributed to indigenous sediment sources, more commonly they are introduced by external point and non-point sources of both natural and man-made origins. Natural origins primarily include formation waters resident in underlying Paleozoic sediments; manmade origins are numerous and include road de-icing chemicals, inorganic fertilizers, urban development, landfills, septic tanks, and animal feedlots.

At the University of Toronto, hydrochemical studies are in progress that aim to develop multi-parameter methods of identifying sources of groundwater contamination. Chemical parameters have included major ions (Ca, Mg, Na, K, Cl, SO_4, NO_3 and HCO_3, minor ions (Br, I, and F), and over 20 trace metals. Tritium has been used locally. To date the study has focused on road de-icing chemicals, saline bedrock waters, fertilizers and urban development as the primary external sources of the chloride enrichment. A total of 110 domestic well water samples, 40 contaminant samples and 70 interstitial water samples have been collected and analyzed.

Much of the completed work has been aimed at determining the natural background levels of major, minor and trace chemical constituents in naturally evolving uncontaminated groundwaters. In addition attempts have been made to characterize chemically the major sources of contamination in the area and, more importantly, to develop an understanding as to how the chemical characteristics of the contaminants are modified during transport through the shallow sub-surface. In previous work, the minor inorganic anions (I and F) have proved to the most reliable indicators of chloride origin, being particularly effective at distinguishing between bedrock and road de-icing chemicals as sources of saline water. In this work, which focuses on trace metal chemistry, few of the determinands have shown anomalously high concentrations in the chloride enriched groundwaters. Nevertheless, there is good evidence that Al, Ni , Ba, Cu, Zn and Pb may prove beneficial indicators of contaminant origin in specific situations.

INTRODUCTION

Despite the recent evidence of Kurtz and Morris (1983) the chloride ion is not generally regarded as a harmful constituent of water. Nevertheless its high solubility, chemically conservative behaviour and virtually ubiquitous association with hazardous chemicals give it the distinction of being a powerful and frequently used indicator of groundwater contamination. In southern Ontario, groundwaters from shallow aquifer systems regularly exhibit chloride ion concentrations in excess of 10 to 15 mg/L which is the anticipated background concentration in naturally evolving groundwaters (Howard, 1985). In many cases chloride levels exceed the maximum desirable concentration of 250 mg/L (MOE, 1984). While in some cases the elevated chloride concentrations can possibly be attributed to very local indigenous sediment sources, more commonly they are introduced by external point and non-point sources of both natural and man-made origins. Natural origins primarily include formation waters resident in underlying Paleozoic sediments; manmade origins are numerous and include road de-icing chemicals, inorganic fertilizers, urban development, landfills, septic tanks, and animal feedlots (Howard et al., 1985).

In recent years the Groundwater Research Group at the University of Toronto has been engaged in a series of studies aimed at understanding the distribution, origins and behaviour of local shallow groundwaters containing elevated concentrations of chloride. The work is phased over three years and considerable data collection and analysis remain to be done. However, the ultimate, long-term objectives of the project are essentially

a) to determine natural background levels of specific major, minor and trace chemical constituents in local shallow groundwaters and to develop convenient multi-parameter methods of identifying sources of groundwater contamination;

b) to confirm that non-point source contaminants such as road de-icing chemicals and products of urban development are accumulating in the sub-surface environment, to determine their chemical behaviour and rates of chemical migration and to evaluate the magnitude and regional extent of the problem.

Much of the completed work has been aimed at determining the natural background levels of major, minor and trace chemical constituents in naturally evolving uncontaminated groundwaters. In addition attempts have been made to characterize chemically the major sources of contamination in the area and, more importantly, to develop an understanding as to how the chemical characteristics of the contaminants are modified during transport through the shallow sub-surface. Parts of the study previously published have demonstrated the value of major anions as indicators of specific contaminant sources. This current paper concerns more recent work which has focused primarily on trace metal geochemistry. It describes the technical approach adopted for the study and summarizes some of the progress achieved. A location map showing the primary areas of investigation is shown on Figure 1.

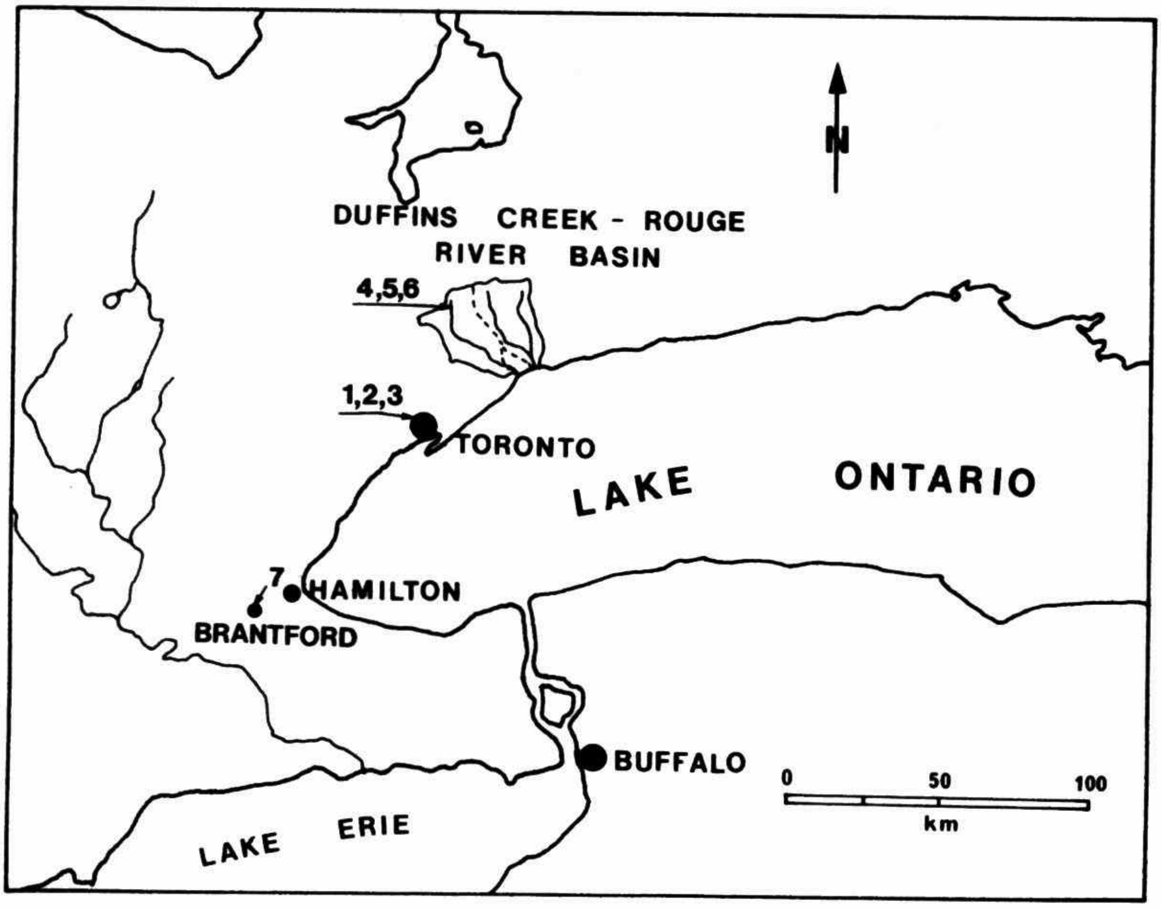


Figure 1. Location map for seven auger sites

APPROACH AND ANALYTICAL PROCEDURES

To date the study has focused on road de-icing chemicals, saline bedrock waters, fertilizers and urban development as the primary non-point sources of the chloride enrichment (Pilon and Howard, 1986 in press). A total of 110 domestic well water samples, 40 contaminant samples and 70 interstitial water samples have been collected and analyzed for a wide range of inorganic parameters. These include the major ions (Ca, Mg, Na, K, Cl, SO_4, NO_3 and HCO_3, minor ions (Br, I, and F), and over 20 trace metals. Tritium has been used locally.

Analytical procedures for pH, anions and major cations are summarized in Table 1. Several of the parameters together with all the trace metals were determined using the ARL 34000 inductively coupled plasma atomic emission spectrometer (ICP-AES) which is capable of providing rapid and simultaneous analysis of up to 31 elements. For this study, a total of twenty-two elements were selected for analysis; these are listed in Table 2 along with the instrument determination limit (5x theoretical detection limit).

Table 1. Analytical Methods for pH, Anion and Major Ion Analysis

Chemical Parameter	Analytical Method
pH	Specific ion electrode potentiometry
NO_3, F	Specific ion electrode potentiometry
Cl	Specific ion electrode potentiometry/ Potentiometric titration
I, Br	Colorimetry
SO_4	Colorimetry/ICP
HCO_3	Titration
Ca, Mg	ICP/Atomic absorption spectrophotometry
K, Na	Flame emission spectrophotometry

Each suite of samples submitted to the ICP laboratory was accompanied by a blank sample consisting of double deionized water which was filtered and prepared in a manner identical to the groundwater samples. The blank was used as an indicator of the amount of contamination introduced to the sample during laboratory preparation. A total of six blanks were submitted for trace element analysis and the results are shown in Table 3. For each element the average value of the blanks was determined and compared to the determination limit. For the twenty-two elements measured by ICP-AES, only five elements Fe, Mg, Ca, Cu, and Ba, exceeded the determination limit. As a result, corrections were made to these analyses. In addition to the blanks, NBS standards were also submitted for ICP checks.

To improve levels of determination using the ICP-AES, sample volumes in excess of 100mL were pre-concentrated prior to analysis. Approximately 100 mL of acidified, filtered water was boiled almost to dryness in a pyrex beaker. 0.5 mL of Ultrapure nitric acid and 1 mL of double distilled water were added to the beaker and the sample was once again evaporated to near dryness. In the final step, 0.5 mL of ultrapure nitric acid and 1 mL of double distilled water were added to the beaker and the sample was evaporated for approximately 5 minutes. Sample volume was then made to 10 mL in a 10 mL erlenmeyer flask.

Table 2. Parameters determined by ICP-AES analysis

Element Units	T.D.L. (mg/L)	D.L. (mg/L)	Element Units	T.D.L. (mg/L)	D.L. (mg/L)
Be	0.00029	0.001	Ca	0.0014	0.007
Ba	0.00025	0.001	Zn	0.004	0.02
Fe	0.0012	0.006	Cu	0.0023	0.0115
Cr	0.0024	0.012	Sb	0.0377	0.1885
S	0.0132	0.066	Pb	0.0460	0.23
Mg	0.0137	0.0685	Cd	0.0032	0.016
As	0.0226	0.113	Co	0.0034	0.017
V	0.0016	0.008	Ni	0.0137	0.0685
Se	0.0823	0.2115	P	0.0357	0.1785
Mo	0.0068	0.034	B	0.0045	0.0225
Al	0.0164	0.082	Mn	0.0006	0.0030

T.D.L.= Theoretical Detection Limit D.L = Determination Limit

Table 3. Results of Trace Element Analysis for Blanks

Element	Ave. of Six Blanks	5X T.D.L.	Element	Ave. of Six Blanks	5X T.D.L.
Be	0.0003	0.001	Ca	0.2691	0.0070
Ba	0.0020	0.001	Zn	0.0152	0.0200
Fe	0.0531	0.0060	Cu	0.0191	0.0115
Cr	0.0045	0.0120	Sb	0.0384	0.1885
S	0.0205	0.0660	Pb	0.0257	0.2300
Mg	0.0846	0.0685	Cd	0.0008	0.0160
As	0.0177	0.1130	Co	0.0027	0.0170
V	0.0056	0.0080	Ni	0.0139	0.0685
Se	0.0374	0.2115	P	0.0758	0.1785
Mo	0.0011	0.0340	B	0.0045	0.0225
Al	0.0594	0.0820	Mn	0.0001	0.0030

SAMPLING - PURPOSE AND PROCEDURES

Uncontaminated Well Waters

A primary focus of recent work has been to determine background levels of anion, major cation and trace constituents in naturally evolving uncontaminated groundwaters. These data are essential if contamination is to be clearly recognised and chemically characterised. This part of the study is being conducted in the Rouge River-Duffins Creek drainage basins (Sibul et al., 1977) where Beck (1985), Thompson et al. (1985), and Howard and Beck (1986) have provided a comprehensive major ion classification of shallow groundwaters. On the basis of this earlier work background concentrations of several major ion parameters were already apparent (Howard, 1985), and potential sampling sites were well documented.

Samples were collected from 110 of the 269 sites sampled by Beck (1985). Since both major ion and trace constituents were to be measured, two well water samples were obtained from each sample location. These were collected in 250 mL polyethylene bottles which had been prepared by rinsing in a 10 per cent nitric acid bath and thoroughly flushed with distilled water. One 250 mL sample was immediately filtered and acidified in the field for trace constituent analysis. Filtering was carried out under pressure using a 0.45 um cellulose acetate filter membrane and a hand pump. To avoid potential contamination by the membrane this was washed with 0.1 per cent ultrapure nitric acid and rinsed 3 times in double distilled water prior to use.

Potential Contaminant Sources

In an attempt to determine the geochemical characteristics of various contaminant sources in the region a wide range of samples were collected. A site map showing sample locations is shown on Figure 2. Part of this work was undertaken in cooperation with Hunter and Associates (Hunter and Associates, 1985) and has been published by Beck and Howard (1986). The types of sample included:

i) 8 samples of road salt (NaCl) from 4 different suppliers (Table 4);
ii) 4 samples of inorganic fertilizer from C.I.L. in Courtright, Ontario (including mono- and di- ammonium phosphate, prilled urea, and ammonium nitrate);
iii) 9 samples of human and livestock sludge obtained from liquid holding tanks, manure pits and manure spreaders;
iv) 5 landfill leachates obtained from collection systems at the Mountain Road, Glenridge Quarry and Brock West Landfill sites;
v) 14 samples of groundwater from southern Ontario bedrock locations.

Prior to chemical analysis, liquid sludge and leachate samples were processed using centrifuge and pressure filtration techniques to separate the liquid fraction. For ICP-AES analysis the samples were then acidified using Ultrapure nitric acid. Solid samples such as fertilizers and road salts were simply dissolved and acidified. In some cases the resulting solutions required considerable dilution due to extremely high sodium concentrations. Samples highly enriched in sodium (> 20,000 mg/L) tend to inhibit the nebulizer function in the ICP-AES to the extent that measurement of other elements becomes unreliable.

Table 4. Road De-icing Chemicals

Sample No.	Location	Source	Formation	Age
18, 22	Windsor,Ont.	Ojibway Mine	Salina	Silurian
19, 23	Goderich,Ont.	Goderich Mine	Salina	Silurian
21, 25	Esterhazy,Sask.	Potash Mine	Prairie	M. Devonian
20, 24	Cleveland,Ohio.	Cleveland Mine	Salina	Silurian

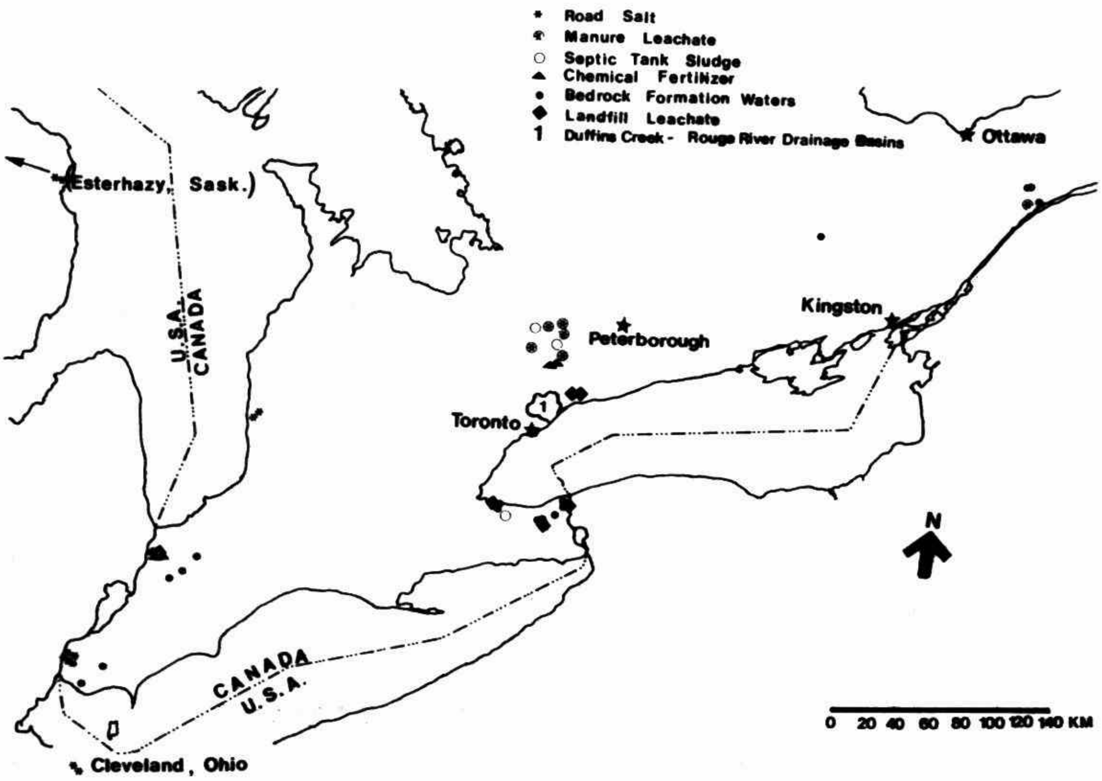


Figure 2. Contaminant source location map

Interstitial Water Samples

While it may be possible to geochemically characterise the contaminants at source, most contaminants will undergo various geochemical transformations during sub-surface transport and ground water mixing. For example, while the gross impact of urban development on groundwater quality was recognised during the early stages of the project following a comprehensive survey of spring waters emanating along the Scarborough Bluffs (Howard et al., 1985; Pilon et al., 1985), specific sources of the contamination were not immediately apparent from the data. Thus in order to investigate more rigorously the degree and hydrogeochemical nature of contamination by urban development and similar non-point contaminant sources, an interstitial water sampling program was implemented involving a total of 20 holes at 8 sites. These sites are listed in Table 5 and are shown on the study area map in Figure 1.

Table 5. Auger Sites

Site	Location	Number of Auger Holes	Contaminant
1	Don Valley adjacent to the Parkway	8	Urbanization/ Road Salt
2	Don Valley-Seton Park	2	Urbanization/ Road Salt
3	Don Valley-Snow Dump	5	Urbanization/ Road Salt
4	Milliken	3	Fallow field/ Control Site
5	Ballantrae-Hwy 48	2	Road Salt
6	Markham	1	Cropland Nitrogen Fertilizer
8	Brantford	3	Cropland Nitrogen Fertilizer

The interstitial waters were extracted from sediment samples collected from the unsaturated zone above the water table. A gasoline powered auger, Dig-R-Mobile, was used to drill to the desired sample depth. The auger rods were then removed and a hand operated auger was used to obtain a partially saturated sediment sample. This sample was placed in a polyethylene bag, sealed, labelled, and packed in ice for transport to the laboratory. Interstitial water was extracted from the sediment samples with minimum delay (usually beginning the same day as collection) so as to avoid changes in the composition of the water (Barber et al., 1977). This was achieved by centrifuging the samples in specially designed Nalgene cups for 30 to 60 minutes at a speed of 2500 to 3500 rpm and a temperature of 4°C. The volume of interstitial extracted depends on the period of centrifugation, weight of sample, pore size distribution of the material, the degree of initial saturation, and the centrifuge dimensions (Edmunds and Bath, 1976). In general, interstitial water recoveries varied between 10 and 350 mL per depth sampling increment. Occasionally samples produced less than 1 mL and could not be used for analytical purposes.

To obtain information regarding the geochemical composition of sediments sampled, a total of thirty-five soil samples were collected for neutron activation analysis. Both short and long lived isotopes were measured and these are listed in Table 6.

Table 6. Elements determined during Neutron Activation Analysis of the Sediments

Short-lived Isotopes	Long-lived Isotopes
Ba	Fe
Ti	Sb
Mg	Br
Na	Cr
Cl	Zn
Al	
Ca	
Mn	
V	

RESULTS AND DISCUSSION

Introduction

With one field season remaining, several elements of the investigation await completion. Furthermore, whilst a considerable volume of chemical data has been collected, many samples remain to be analyzed and the currently available results are in various stages of processing, plotting and interpretation. Thus while substantial progress has been achieved during the study, it must be emphasised that the results presented and discussed below are preliminary and may be subject to refinement and possible revision as further data become available.

Background Chemistry of Uncontaminated Groundwaters

The background chemistry of uncontaminated waters will vary according to the chemistry of the input water (aquifer recharge), the geochemistry of the aquifer matrix and the degree of hydrochemical evolution the water undergoes as it moves through the system. Early studies aimed at understanding the hydrochemical evolution of groundwaters in surficial sediments were initiated by Beck (1985) and have been extended as part of the present investigations.

Major and Minor Ions

The work of Beck (1985) focused on major and minor ion parameters. This and subsequent work (Howard, 1985; Howard and Beck, 1986) showed that ground waters migrating regionally in shallow unconsolidated sediments of southern Ontario evolved from a Type 1A through 2A and 3A to a Type 4A water with cation exchange as the primary modifying influence. During this chemical evolution, dissolution of indigenous soluble salts, a commonly recognised process in large sedimentary basins, was found to have only minor importance. Table 7 shows typical background concentrations of major and minor ion constituents in uncontaminated Type 1A through Type 4A groundwaters of the Duffins Creek / Rouge River drainage basins. The data suggest that chloride concentrations as low as 15-20 mg/L (above the maximum levels observed) may be regarded as a positive indication of contamination.

Table 7. Typical Major and Minor Ion Background Hydrochemistry of Naturally Evolving Groundwaters

		EVOLVING WATER TYPE			
		1A	2A	3A	4A
Parameter	Unit				
Ca	mg/L	90	40	30	20
Mg	mg/L	20	20	15	10
Na	mg/L	5	20	30	50
K	mg/L	2	2	2	2
HCO_3	mg/L	350	250	250	250
Cl	mg/L	<5	<10	<15	<15
SO_4	mg/L	20	5	5	5
NO_3	mg/L	<10	<10	<10	<10
F	mg/L	<0.2	0.2	0.25	>0.25
I	mg/L	<0.005	<0.01	<0.02	>0.015

Trace Metals

With respect to trace constituents, Tables 8a, 8b and 8c present a statistical summary of the trace metal data for the presumed uncontaminated 1A, 2A and 3A groundwaters. Since the occasional anomalous trace constituent analysis can result in a distorted mean concentration and relatively high standard deviation, the general practice has been to use median values and ranges to compare water types. There are currently insufficient data to characterise confidently the trace metal content of Type 4A waters.

Type 1A waters which represent the younger, recharge waters tend to display lower concentrations of most trace constituents relative to the older waters 2A and 3A. Minor exceptions include Al, Fe, and Ba which occasionally show elevated concentrations. With the exception of Fe and Mn, all trace constituents present above determination limits, occur below either the maximum acceptable (MAC) or the maximum desirable (MDC) concentrations as recommended by the Ontario Ministry of the Environment (MOE, 1984). All Type 1A waters exceeded the MDC limit of 0.3 mg/L for Fe and one sample exceeded the MDC limit of 0.05 mg/L for Mn.

Type 2A waters which are older than Type 1A, but pre-date Types 3A and 4A, contain concentrations of trace elements which generally fall between those of 1A and 3A. Type 2A waters show slightly higher (median) concentrations of Mn, P, Cu, and B relative to Type 1A waters. Concentrations of Al, Fe, and Ba in these waters are lower than in Type 1A waters.

Type 3A waters contain elevated concentrations of Mn, P, Mo, Cu, and B relative to Type 1A and 2A waters. These waters also show concentrations of Fe and Al similar to those of Type 1A waters. Mn concentrations were highest in Type 3A groundwaters (ranging from 0.0319 to 0.2363 mg/L) with 4 of 6 samples exceeding the MDC of 0.05 mg/L for Mn. In addition, 3 of the 6 Type 3A samples exceeded the MDC of 0.3 mg/L for Fe.

In summary, two general trends can be identified in the uncontaminated groundwaters during transition from Type 1A to 3A waters. These are as follows:

a) increasing P, Mn, Mo, Cu, and B concentrations; and,

b) decreasing Ba concentrations.

In all three water types concentrations of Ni, Pb, As, Se, Sb were found to occur at concentrations less than the determination limit.

Table 8a Statistical Data for Type 1A Groundwaters

Element	N	$\bar{x}$	σ	range	median
Mn	3	0.0480	0.0419	0.0131-0.1070	0.0241
P	3	<0.0178	--	<0.0178-0.0323	<0.0178
Mo	3	<0.0034	--	<0.0034	<0.0034
Al	3	<0.0082	--	<0.0082-0.1461	<0.0082
Zn	3	0.1797	0.2338	0.0094-0.5103	0.0193
Ni	3	<0.0068	--	<0.0068	<0.0068
Fe	3	0.4863	0.1802	0.3580-0.7412	0.3597
Pb	3	<0.023	--	<0.023	<0.023
Cu	3	0.0238	0.0122	0.0083-0.0382	0.0249
Co	3	<0.0017	--	<0.0017	<0.0017
Cr	2	0.0023	0.0021	0.0002-0.0043	0.0029
Cd	3	<0.0016	--	<0.0016	<0.0016
As	3	<0.0113	--	<0.0113	<0.0113
Se	3	<0.0211	--	<0.0211	<0.0211
Sb	3	<0.0188	--	<0.0188	<0.0188
V	3	0.0015	0.0007	0.0008-0.0025	0.0011
B	3	<0.0001	--	<0.0001	<0.0001
Ba	3	0.0941	0.0487	0.0258-0.1361	0.1203
Be	3	<0.0001	--	<0.0001-0.0008	<0.0001

-- Not Calculated Units mg/L

Table 8b Statistical Data for Type 2A Groundwaters

Element	N	$\bar{x}$	σ	range	median
Mn	3	0.0310	0.0035	0.0276-0.0357	0.0296
P	3	0.0512	0.0328	0.0273-0.0976	0.0288
Mo	3	<0.0034	--	<0.0034	<0.0034
Al	3	0.0114	0.0062	0.0038-0.0191	0.0115
Zn	3	0.1578	0.1536	0.0074-0.3687	0.0974
Ni	3	<0.0068	--	<0.0068	<0.0068
Fe	3	0.3095	0.2444	0.0180-0.6160	0.2946
Pb	3	<0.023	--	<0.023	<0.023
Cu	3	0.0242	0.0180	0.0069-0.0490	0.0167
Co	3	<0.0017	--	<0.0017	<0.0017
Cr	3	<0.0012	--	<0.0012-0.0005	<0.0012
Cd	3	<0.0016	--	<0.0016	<0.0016
As	3	<0.0113	--	<0.0113	<0.0113
Se	3	<0.0211	--	<0.0211	<0.0211
Sb	3	<0.0188	--	<0.0188	<0.0188
V	3	0.0017	0.0010	0.0010-0.0031	0.0010
B	3	0.0283	0.0051	0.0213-0.0333	0.0303
Ba	3	0.1240	0.0253	0.1019-0.1595	0.1019
Be	3	<0.0001	--	<0.0001-0.0002	<0.0001

-- Not Calculated Units mg/L

Table 8c Statistical Data for Type 3A Groundwaters

Element	N	$\overline{x}$	σ	range	median
Mn	6	0.0949	0.0703	0.0319-0.2363	0.0581
P	6	0.1676	0.0970	0.0508-0.3591	0.1493
Mo	2	0.0090	0.0053	0.0037-0.0143	0.0090
Al	4	0.0504	0.0197	0.0191-0.0745	0.0538
Zn	6	0.0666	0.0690	0.0031-0.2010	0.0455
Ni	6	<0.0068	--	<0.0068	<0.0068
Fe	6	0.3833	0.2061	0.0603-0.6080	0.4154
Pb	6	<0.023	--	<0.023	<0.023
Cu	6	0.0471	0.0405	0.0105-0.1267	0.0351
Co	6	<0.0017	--	<0.0017	<0.0017
Cr	6	<0.0012	--	<0.0012-0.0129	<0.0012
Cd	6	<0.0016	--	<0.0016	<0.0016
As	6	<0.0113	--	<0.0113	<0.0113
Se	6	<0.0211	--	<0.0211	<0.0211
Sb	6	<0.0188	--	<0.0188	<0.0188
V	6	0.0011	0.0004	0.0008-0.0019	0.0009
B	6	0.0870	0.2080	0.0473-0.1137	0.0905
Ba	6	0.1970	0.2355	0.0685-0.7161	0.0836
Be	6	<0.0001	--	<0.0001	<0.0001

-- Not Calculated Units mg/L

Contaminant Sources

A total of 43 potential contaminants were submitted for major and minor ion analyses, while 17 were submitted for trace constituent analysis. Samples submitted for trace constituent analysis included 1 landfill leachate, 9 bedrock waters, 4 inorganic fertilizers and 3 road de-icing chemicals. Site locations are shown on Figure 2. The major, minor and trace chemistry of each contaminant is discussed below.

Road De-icing Chemicals

A 5 % solution of NaCl road de-icing chemical was found to contain 20,250 mg/L Na, 30,860 mg/L Cl together with minor amounts of SO$_4$ (222 mg/L) and Ca (62.5 mg/L). The 5 % solution of CaCl$_2$ road de-icing chemical contained 12,890 mg/L Ca, 25,892 Cl with minor associated amounts of Na (550 mg/L) and SO$_4$ (25.8 mg/L). Both the NaCl and the CaCl$_2$ displayed similar trace element impurities as shown in Table 9. The 5 % solution of sodium chloride is distinguished from the bedrock waters, leachate and inorganic fertilizers (see below) by elevated concentrations of Al, Ni, Fe, Cu, and Ba. Likewise, CaCl$_2$ (5 % solution) also contains similar elevated concentrations of Ni and Fe but is distinguished from NaCl by lower concentrations of Al and Ba and a considerably higher concentration of Cu. Concentrations of Mn, Pb, Co, Cr, Cd, Se, Sb, B, V, As, Zn, P and Be were below ICP-AES determination limits for both the NaCl and $CaCl_2$ chemicals.

Table 9 Trace Constituents in Chemical Road De-Icing Chemicals

Element	NaCl 5 % Solution (mg/L)	$CaCl_2$ 5 % Solution (mg/L)
Al	166.7-181.0	92.1
Ni	42.3- 58.9	57.9
Fe	42.2- 58.8	57.8
Cu	98.2-154.5	251.9
Ba	7.4- 15.9	4.8

Fertilizers

The four inorganic fertilizers analyzed (mono- and di- ammonium phosphates, prilled urea, and ammonium nitrate) were found to exhibit considerable variations in their major and minor ion chemistry most likely due to the fact that each fertilizer is made to replace specific macro- and micronutrients in the soil. For example, nitrate concentrations vary from 26 mg/L in the prilled urea to 35,000 mg/L in the ammonium nitrate, while mono- and di- ammonium phosphate fertilizers contain notably elevated concentrations of Na (112 - 143.75 mg/L) and SO_4 (1772.6 - 3220 mg/L). Chloride concentrations were generally found to be low (typically <10 mg/L) although di-ammonium phosphate did show a concentration of 36 mg/L.

The four inorganic fertilizers also exhibit varying concentrations of trace constituents. As would be expected, mono- and di- ammonium phosphate fertilizers are distinguished from all other analysed contaminants and fertilizers by the presence of elevated concentrations of P (10^3 mg/L). These fertilizers also show elevated concentrations Mo and Cr. By comparison, ammonium nitrate and prilled urea are characterised by elevated concentrations of Al, Se, and Sb.

Landfill Leachate

As expected, the five landfill leachates submitted for major and minor ion analysis contain elevated concentrations of Cl (between 480 and 685 mg/L) and NO_3 (between 26.5 and 145 mg/L). As such, these leachates are readily distinguished from road de-icing chemicals and inorganic fertilizers, neither of which would normally exhibit high concentrations of both anions. More surprising are the relatively low levels of trace metals found in the leachates (Table 10). Leachate sampled from the gatehouse well in the Mountain Road Landfill site (Table 10) was found to contain very low levels of P, Zn, Fe, and As relative to the other contaminants investigated. Trace constituents Mn, Mo, Al, Ni, Pb, Co, Cr, Cu, Cd, Be and V were all below determination limits. The trace constituents present in highest concentrations were B (1.45 mg/L) and Ba (.1098 mg/L) but these concentrations are comparable to those present in bedrock waters sampled from domestic wells.

Table 10 Trace Constituents in Landfill Leachate

Element	Typical Landfill Leachate Composition+ (mg/L)	Mountain Rd. Landfill Leachate Composition (mg/L)
As	0.038	0.1140
Al	0.27	<0.0082
Ba	0.08	0.1078
Be	0.025	<0.0001
B	4.5	1.4552
Cd	0.0037	<0.0016
Cr	0.053	<0.0012
Cu	0.024	<0.0012
Fe	24	<0.0006
Pb	0.054	<0.023
Mn	0.6	<0.0003
Mo	0.013	<0.0034
Ni	0.069	<0.0068
V	**	<0.0008
Zn	0.5	0.0239

** Not Detected   + Daniel and Liljestrand (1984)

Bedrock Waters (Domestic Wells)

Low permeability bedrock formations commonly contain groundwaters with elevated major and minor ion concentrations. Southern Ontario is no exception. Occasionally groundwaters from bedrock formations leak into overlying surficial sediments where they cause contamination. To date, sampling of bedrock waters has been largely restricted to deep domestic wells where groundwater salinities tend to be unrepresentatively low. Nevertheless, some samples have shown Cl concentrations as high as 966.54 mg/L with Na up to 562.5 mg/L. SO_4 concentrations in the bedrock waters are generally low (31.6-34.3 mg/L) which may be a consequence of sulphate reduction. This conclusion appears to be supported by moderate to high concentrations of Mn (0.0469 - 4.8031 mg/L) and Fe. In general Zn, B and Ba are present in concentrations which are higher than landfill leachates but lower than other contaminants. The trace constituents P, Mo, Al, Ni, Pb, Co, Cr, Cd, As, Se, Sb, Be, Cu, and V are present in concentrations below determination limits for these elements.

Interstitial Waters

Urban road sites

The study of interstitial waters at urban road sites has revealed considerable contamination by road de-icing chemicals and other products of urban development. As shown in Figures 3 and 4 these waters may contain between 10^3 and 10^4 mg/L Cl and 10^3 mg/L Na as compared to concentrations of less than 10^2 mg/L Cl and less than 10^2 mg/L Na for interstitial waters from rural road sites. The elevated concentrations of Na and Cl are comparable to the concentrations of Na and Cl in seawater (10,500 mg/L and 19,000 mg/L respectively). One sample located approximately 100 m downslope from a ramp on the Don Valley Parkway

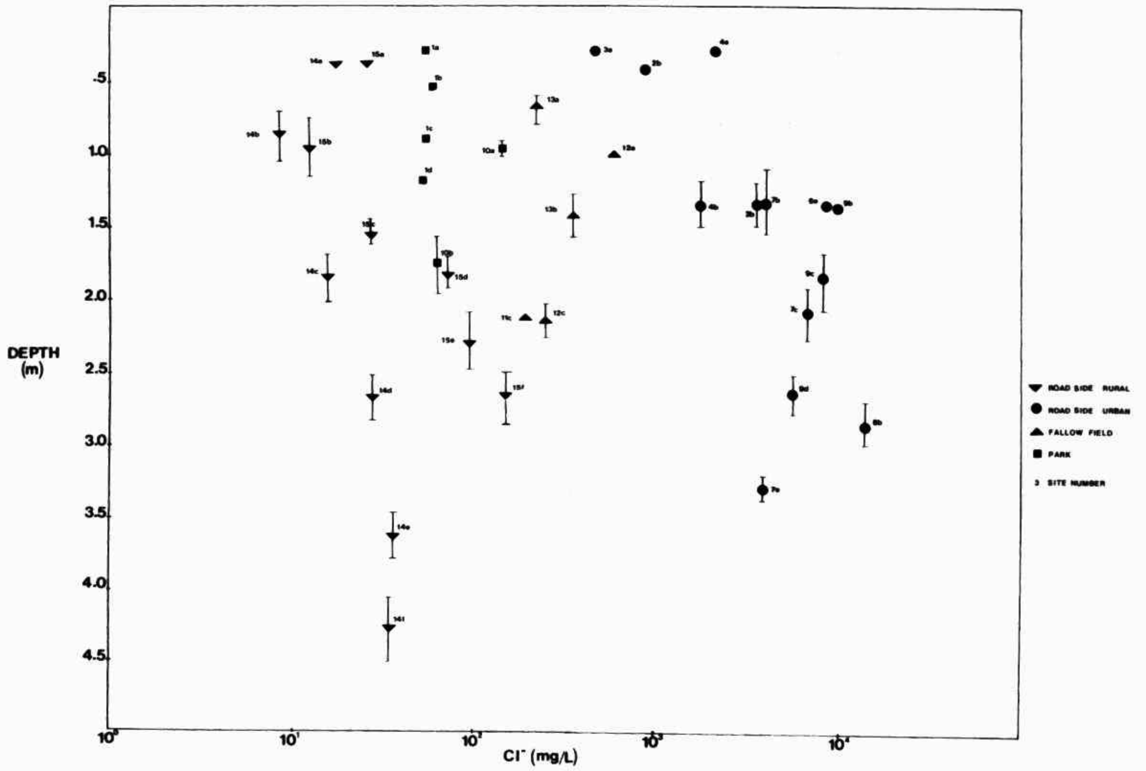


Figure 3. Plot of chloride concentration vs. depth

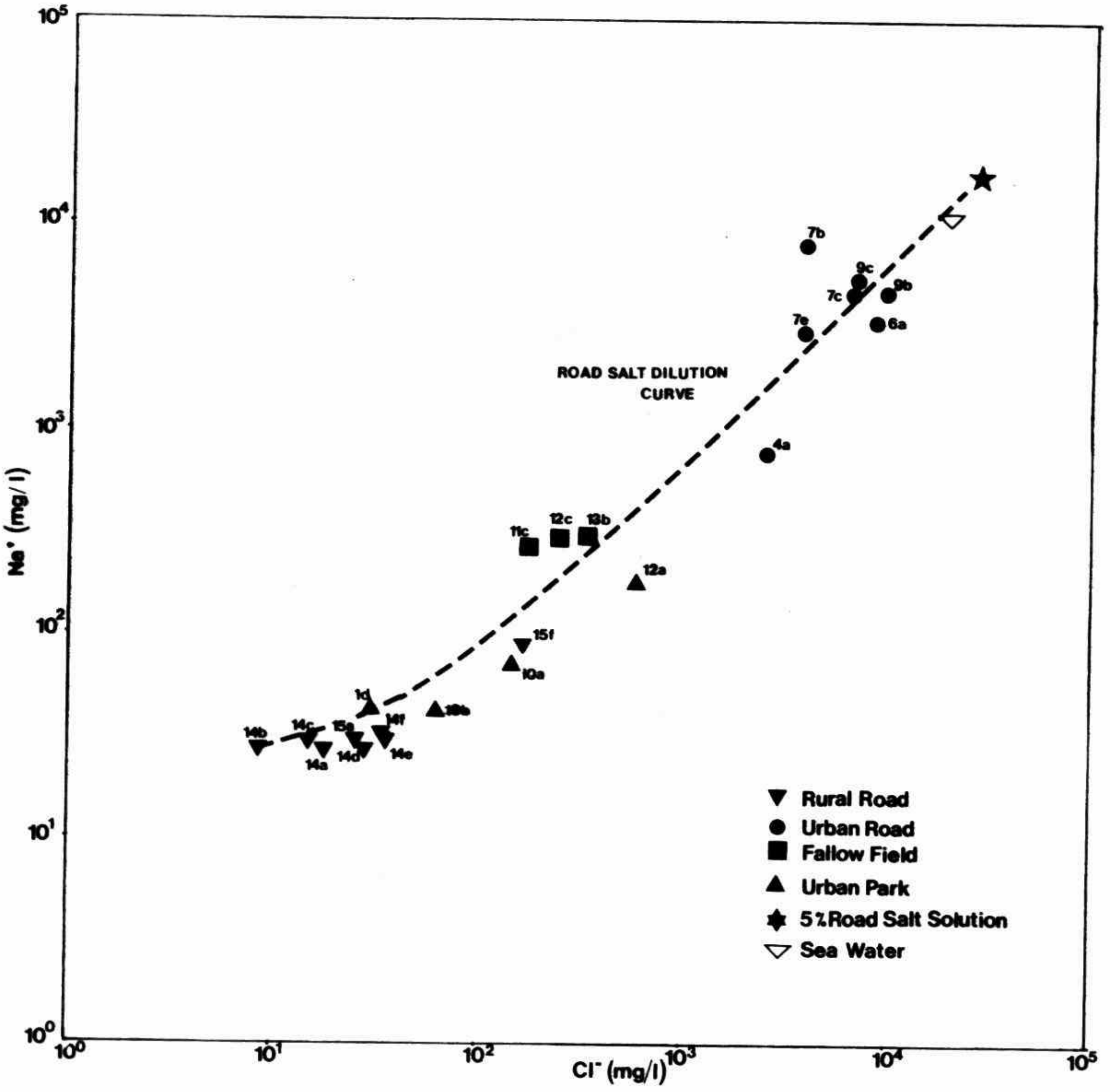


Figure 4. Plot of chloride vs sodium concentration

at a depth of 2.85m contained chloride in excess of 13,000 mg/L. Extremely elevated chloride levels were measured in interstitial waters sampled as deep as 3.3m below the surface.

Trace constituent analyses of interstitial water samples from urban road sites (Table 11) reveal elevated concentrations of Mn, P, Al, Fe, Pb, Cr, As, Se, Sb, Ba relative to all other study sites. Comparison to Table 9 suggests that while road de-icing chemicals may account for enrichment in Al, Fe and Ba other factors must be responsible for the elevated concentrations of the other elements.

Table 11 ICP-AES Results for Site Representative Samples (Units mg/L)

Site Sample	Cropland (25A)	Fallow Field (11B)	Rural Road (15C)	Snow Dump (8A)	Urban Road (7E)	Parkland (10A)
Mn	0.0312	0.0067	0.0121	0.6012	0.1566	0.0389
P	0.2412	0.1297	0.1853	2.4199	2.4199	0.1326
Mo	<0.0034	0.0004	0.0052	0.0319	0.0099	0.0081
Al	0.1334	0.0641	0.1137	17.8170	0.0819	0.0299
Zn	0.0983	0.0183	0.0492	0.4995	0.0370	0.0125
Cd	<0.0016	<0.0016	0.0007	0.0126	<0.0016	<0.0016
As	<0.0113	0.0301	0.0433	0.0915	0.0619	0.0513
Se	<0.0211	0.0432	0.0197	0.0871	0.0564	0.0742
Sb	<0.0188	0.0569	0.0510	0.0846	0.0748	0.0548
V	<0.0008	0.0032	0.0026	0.1443	0.0032	0.0007
Ni	<0.0068	0.0111	0.0211	0.0581	0.0143	0.0123
Fe	0.1440	0.0006	0.0176	61.9589	0.0387	0.0006
Pb	<0.023	0.0147	0.0086	1.8708	0.0161	0.0030
Cu	0.0214	0.0560	0.3540	0.6051	0.2245	0.0207
Co	<0.0017	0.0018	0.0005	0.0096	0.0014	<0.0017
Cr	<0.0012	0.0061	0.0024	0.0713	0.0052	0.0039
B	0.0366	0.0121	0.0166	0.2334	0.1525	0.1068
Ba	0.0391	0.0539	0.0099	0.2535	0.3364	0.0855
Be	<0.0001	0.0001	<0.0001	0.0130	0.0001	0.0001

Urban Snow Dump Site

A similar degree of contamination is seen in interstitial waters sampled from a site where snow removed from city streets and parking lots is dumped. These waters contain elevated concentrations of Cl (10^3 mg/L), Na (10^2 to 10^3 mg/L) and SO_4 (10^2 mg/L) relative to the urban park, and cropland sites. Trace element analyses indicate relatively high concentrations of Mn, P, Al, Zn, Fe, Pb, Cu, Cr, V, B and Be. It is suggested that the enrichment in trace constituents may be related to the source of the snow (Scott, 1979). Snow removed from streets would contain particulates enriched in heavy metals such as Fe, Pb, and Cu. When the snow melts, the particulates remain and accumulate in the soil column. Scott (1979) indicated that dumps receiving their snow from streets had a higher accumulation rate of Na, Cl, and Pb than did those snow dumps receiving their snow from parking lot dumps.

Rural Road Sites

Interstitial waters from the rural road sites contain Cl (10^1 to 10^2 mg/L), Na (10^1 mg/L) and SO_4 (10^1mg/L) concentrations which are considerably lower than those of the urban road site interstitial waters. Trace constituent analyses are comparably low with only P , Al, and Cu displaying significant concentrations. Al and Cu are present in high concentrations of road salts while P is a major constituent of inorganic fertilizers .

Cropland and Fallow Field Sites

Both cropland and fallow field interstitial waters contain similar concentrations of NO_3, K and Ca. However, the fallow field samples contain elevated concentrations of Cl (10^2 mg/L) and Na (10^2 mg/L) as compared with the cropland samples which have Cl and Na concentrations of 10^1 mg/L and 10^1 mg/L respectively. This may be more a reflection of local geological conditions than the nature of the contamination.

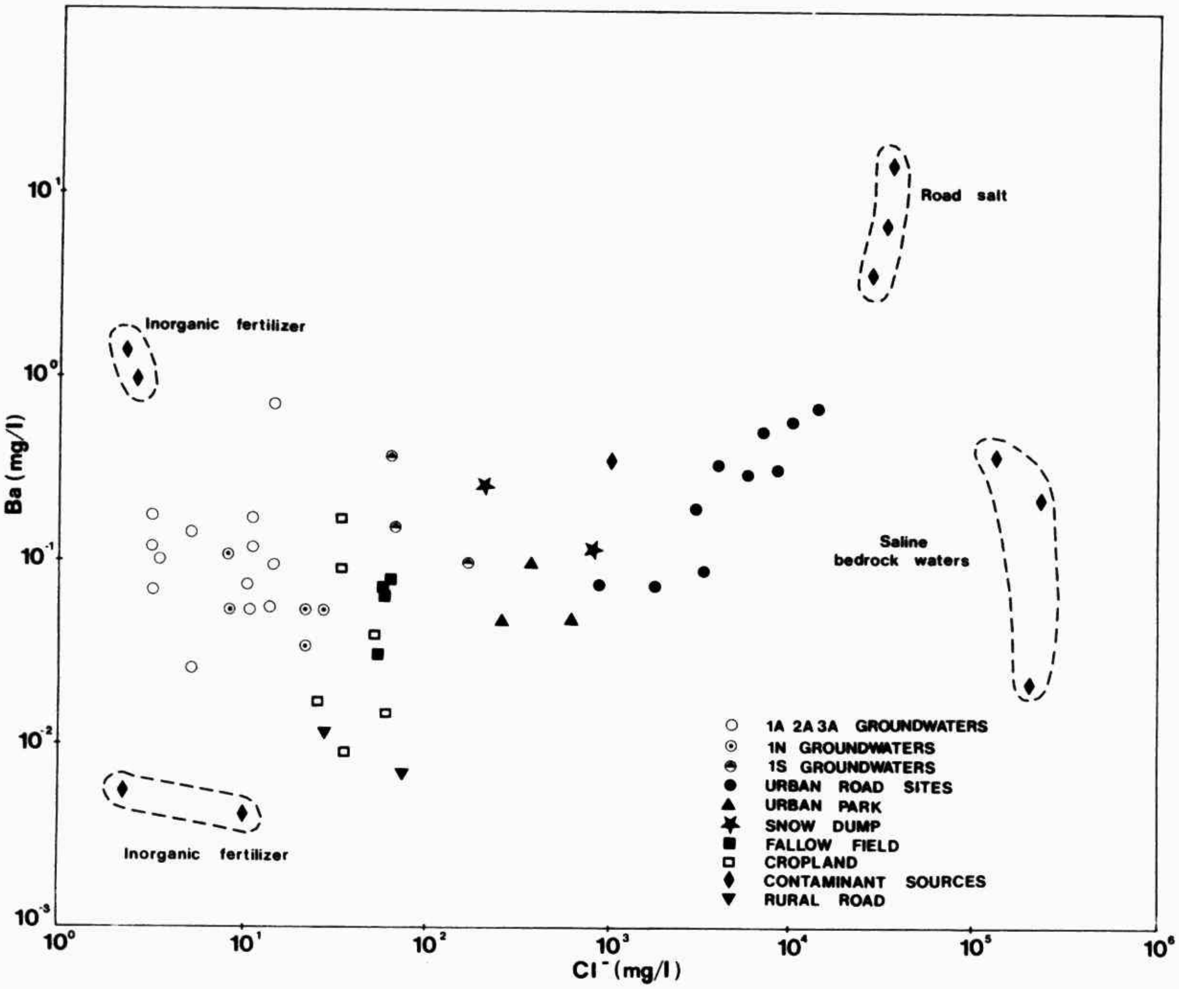


Figure 5. Plot of barium vs chloride concentration

Local geological conditions also play an important role in the geochemical modification of contaminants as they move through the shallow sub-surface. For example, interstitial waters sampled from cornfields contain moderate concentrations of Mn, P, Zn, Fe, Cu, B relative to the other sites investigated, but elements such as Mo and Cr evident in the fertilizers (see above) are not found to be present. This type of process is further illustrated by Figures 5 and 6 which show how concentrations of Ba and Cu in contaminant sources are, in many cases, notably different from concentrations present in the contaminated groundwaters.

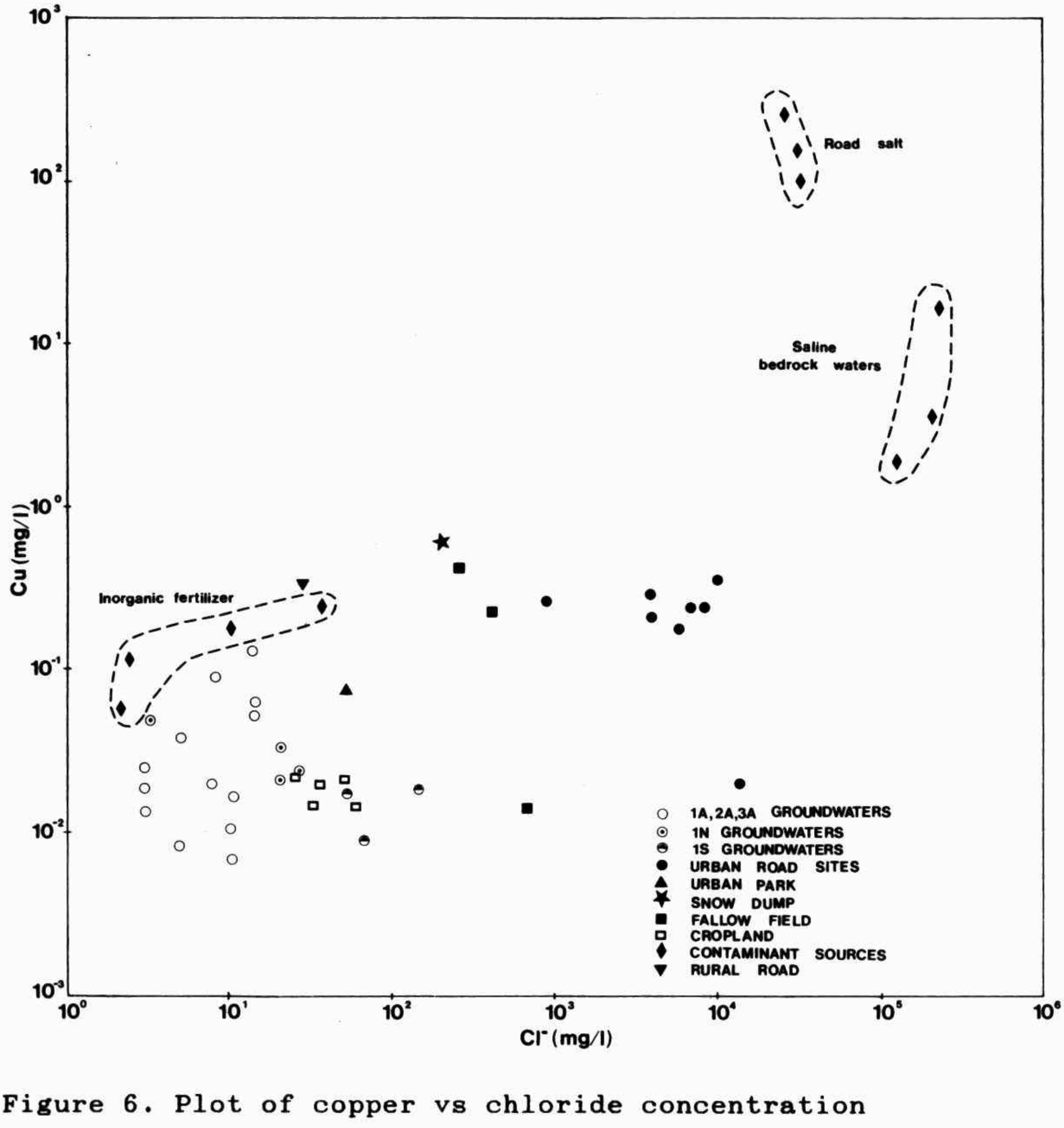


Figure 6. Plot of copper vs chloride concentration

CONCLUDING REMARKS

Shallow aquifer systems in southern Ontario frequently exhibit elevated chloride concentrations that locally exceed water quality guidelines. While in some cases the elevated chloride concentrations can be attributed to indigenous sediment sources, more commonly they are introduced by external point and non-point sources of both natural and man-made origins. Natural origins primarily include formation waters resident in underlying Paleozoic sediments; manmade origins are numerous and include road de-icing chemicals, inorganic fertilizers, urban development, landfills, septic tanks, and animal feedlots.

At the University of Toronto, hydrochemical studies are in progress that aim to develop multi-parameter methods of identifying sources of groundwater contamination. Chemical parameters have included major ions (Ca, Mg, Na, K, Cl, SO_4, NO_3 and HCO_3) minor ions (Br, I, and F), and over 20 trace metals. To date, the study has focused on road de-icing chemicals, saline bedrock waters, fertilizers and urban development as the primary external sources of the chloride enrichment.

Much of the completed work has been aimed at determining the natural background levels of major, minor and trace chemical constituents in naturally evolving uncontaminated groundwaters. These studies have revealed very low concentrations of most trace metals in uncontaminated groundwaters, thus re-inforcing the view that trace metals have the potential to play a role in the detection and source identification of groundwater contamination. Certainly, major ion, minor ion and trace element studies of the various contaminant sources confirm the existence of chemical signatures which can definitively identify contaminant sources. However, in some cases, these signatures are modified by rock-water reactions, and more work is necessary to understand these reactions if trace metal groundwater chemistry is to be as effective as major and minor ions (particularly I and F) in revealing contaminant origins. On the basis of completed work there is good evidence that the elements Al, Ni , Ba, Cu, Zn and Pb may prove most beneficial as diagnostic indicators of contaminant origin in specific cases.

ACKNOWLEDGMENTS

Anion and major cation analyses were carried out by Lucy Molas. Trace constituent analyses were completed by M.A. Balicki at the University of Toronto ICP-AES laboratory. We also wish to thank Mark Hughes who assisted with the augering and collection of sediment samples, and helped considerably with both the sample preparation and data processing. Special acknowledgment goes to Paul Beck (formerly of Hunter and Associates; currently with the M.O.E.) for his continuing support of the University of Toronto Groundwater Research Group. The work is funded by the Ontario

Ministry of the Environment (Project Liaison Officer - Peter McKenna) with additional support from the Natural Sciences and Engineering Research Council.

REFERENCES

Barber, C., Maris, P.J. and Knox, K. 1977. Groundwater sampling: the extraction of interstitial water from cores of rock and sediments by high-speed centrifuge.

Beck, P. 1985. The use of hydrochemistry to classify groundwater types and to interpret ground water flow in Quaternary sediments in South Central Ontario. unpub. M.Sc. Thesis, University of Toronto, 85pp.

Beck, P. and Howard, K.W.F. (1986) The significance of iodide and fluoride in groundwaters from surficial sediments from Southern Ontario. Proceedings of the International Association of Hydrogeologists 3rd Canadian Hydrogeological Conference, Saskatoon, 1986, 56-65.

Daniel, D.E. and Liljestrand, H.M., 1984. Effects of landfill leachates on natural liner systems. Department of Civil Engineering, University of Texas. 86pp.

Edmunds, W.M. and Bath, A.H. 1976. Centrifuge extraction and chemical analysis of interstitial waters. Environmental Science & Technology. 10, 5, 467-472.

Howard, K.W.F. 1985. An approach to recognizing low level contamination of groundwaters in shallow sedimentary aquifers. Water Pollution Research Journal of Canada 20, No. 2, 1-11.

Howard, K.W.F. and Beck, P. (1986) Hydrochemical interpretation of groundwater flow systems in Quaternary sediments of Southern Ontario.C.J.E.S., 23, 938-947.

Howard, K.W.F., Pilon, P.E. and Falck, H., 1985. Regional geochemical stratification of shallow groundwaters resulting from catchment urbanization.Ontario Ministry of the Environment Technology Transfer Conference No. 6, Part2. Water Qual. Research, ISSN 0-825-491, 160-183, Toronto, Dec. 1985.

Hunter and Associates, 1985. A report on differentiating various sources of chloride in domestic well waters. R. and D. Project 22304. MTC. pp.46 (draft).

Ministry of the Environment,1984. Ontario Drinking Water Objectives. 56pp.

Kurtz,T.W., and Morris,R.C., 1983. Dietary chloride as a determinant of "sodium-dependent" hypertension. Science 222, 1139-1140.

Pilon,P.E. and Howard, K.W.F. (1986,in press). Contamination of subsurface waters by road de-icing chemicals. Water Pollution Research Journal of Canada.

Pilon,P.E., Howard K.W.F. and Kaye,B.G., 1985. The influence of urban development on the quality of groundwater beneath

Metropolitan Toronto.98th Annual G.S.A. Abstracts with Programs 17(7), Orlando, Sept.,1985.

Sibul, U., Wang, K.T., and Vallery, D. 1977. Groundwater resources of the Duffins Creek - Rouge River drainage basins. Ontario Ministry of the Environment, Water Resources Branch, Water Resources Report 8. 106pp.

Scott, W.S., 1980. Occurrence of salt and lead in snow dump sites. Water, Air and Soil Pollution. 13. 187-195

Thompson,M.J., Howard, K.W.F. and Beck, P. 1985. Iodide geochemistry of shallow groundwaters in southern Ontario. 98th Annual G.S.A. Abstracts with Programs 17(7),Orlando,Sept.,1985.

TD
172.5
.O57
1986
part C

Proceedings : technology
transfer conference
76021

TECHNOLOGY TRANSFER CONFERENCE
1986

Organized by RESEARCH ADVISORY COMMITTEE
J. Pagel, Chair

Sponsored by CORPORATE RESOURCES DIVISION
A. Castel, Executive Director

CONFERENCE COMMITTEE:

	M. Moselhy	***Co-ordinator***
Environment Ontario:	D. Bartkiw	G. Rees
	W. Chan	R. Reguly
	J. Donnan	G. Ronan
	D. McTavish	C. Schenk
	E. Piché	
Labour Ontario:	G. Wright	
Health Ontario:	L. Smith	
Environment Alberta:	H. Sims	
Environment Québec:	H. Saint-Martin	
Environment Canada:	F. Hurtubise	K. Shikaze
	B. Jank	
University of Waterloo:	J. Cherry	
Lakehead University:	G. Ozburn	
Goodfellow Consult. Inc.:	H. Goodfellow	
Zenon Environmental Inc.:	A. Benedek	

Communications:	T. Gorsline	C. Labonté
Poster Session:	H. Eijsenck	
Spouse Program:	Ann-Marie Clarke	